

The Standardization of Volumetric Solutions

By

R. B. Bradstreet, M. S.

SECOND EDITION

Completely Revised and Enlarged



1944

CHEMICAL PUBLISHING CO., INC.

BROOKLYN, N. Y.

U. S. A.



Copyrighted

1944

CHEMICAL PUBLISHING CO., INC.

BROOKLYN

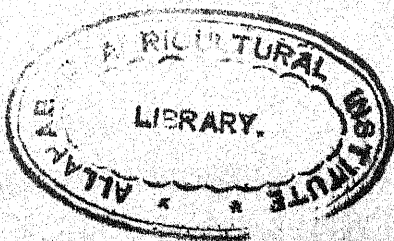
NEW YORK

Foreword

ORDINARILY, a standardized solution is a means to an end and not the end itself. Therefore, a set of good methods for preparing such solutions is very welcome. Analysts, research and other laboratory men have had training in these methods but when they wish to make up a solution, they do not like to spend much time in going through books and journals in order to find the directions for making up the specific one desired. In this book, the author has gathered together methods which have stood the test of laboratory experience, and has described them in a concise manner all ready for rapid laboratory use.

This book is not for the beginner, since it presupposes a general knowledge and practice of analytical chemistry. It is a handy reference work for the man who must hurry to get his results. The discussions of the methods and their good and bad points are short and very useful, and the text is replete with helpful hints, equations, tables of important data, expressions for calculating normalities, etc.

The writer believes that his friend and former asso-



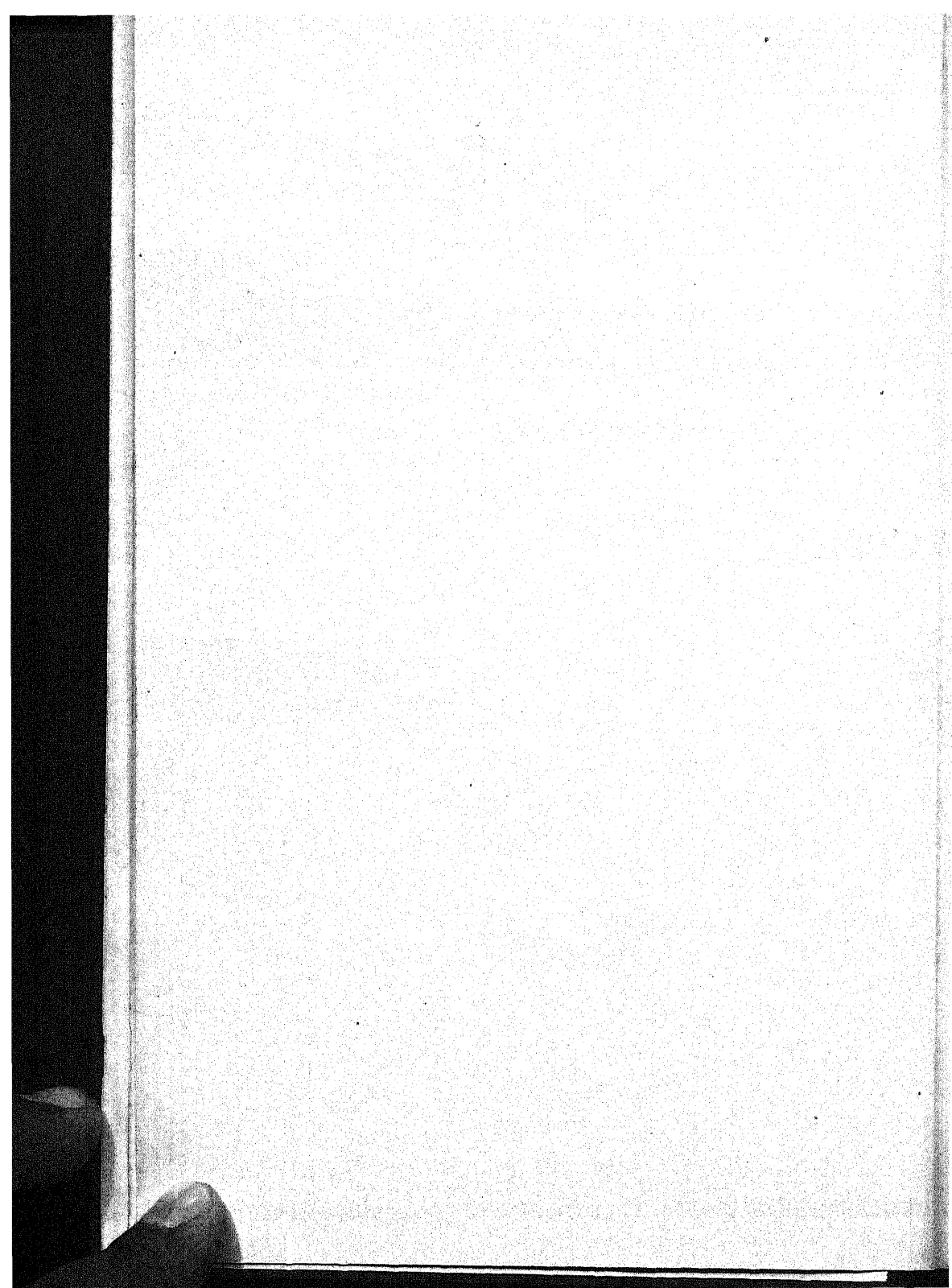
ciate has done his self-appointed task well. His long experience in his chosen field gives him the proper background for such a work and this compilation of good practical methods ought to be of real service.

HARRY L. FISHER

Acknowledgment

THE author wishes to express his thanks to Dr. Harry L. Fisher, U. S. Industrial Alcohol Co., V. L. Burger, General Laboratories, United States Rubber Products Co., and J. B. Lewis, Esso Laboratories, Standard Oil Co. of New Jersey, all of whom contributed helpful criticisms and suggestions.

R. B. BRADSTREET



8-4-46
5263

Table of Contents

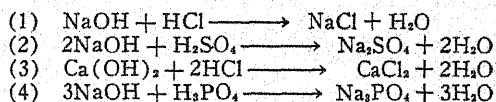
CHAPTER	PAGE
I. GENERAL CONSIDERATIONS	1
II. CALIBRATION OF VOLUMETRIC APPARATUS	11
III. INDICATORS	16
IV. STANDARD SUBSTANCES	31
V. STANDARD SOLUTIONS OF ACIDS AND BASES	48
VI. STANDARD SOLUTIONS OF PRECIPITATION REAGENTS	64
VII. STANDARD SOLUTIONS OF OXIDIZING REAGENTS	71
VIII. MISCELLANEOUS STANDARD SOLUTIONS .	101
STOCK SOLUTIONS OF INDICATORS . . .	112
STOCK SOLUTIONS OF REAGENTS . . .	113
NORMAL SOLUTIONS (Tables)	116
EQUATIONS INVOLVED IN STANDARDIZATION	122

LOGARITHMS OF VOLUMETRIC FACTORS . . .	124
ABSOLUTE DENSITY OF WATER . . .	126
CALIBRATION OF THERMOMETERS . . .	127
LOGARITHMS OF NUMBERS	128
ATOMIC WEIGHTS	146
INDEX	147

CHAPTER I

General Consideration: *Definition of a Normal Solution. Normality and Equivalent Weight. Effect of Temperature and Buoyancy Error. Requirements for Standard Solutions. Calculations. Requirements of an Indicator.*

A NORMAL solution may be defined as a solution of known concentration, a liter of which is equivalent to a gram-atom of hydrogen. A fractional normal solution contains a fractional gram-atom of hydrogen per liter. The equivalent weight is the weight in grams corresponding to one gram-atom of hydrogen. In acid-base reactions, the hydrogen equivalent is easily found, since it is the number of titratable hydrogen atoms, thus:



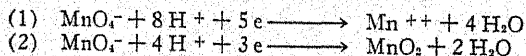
The equivalent weight of either NaOH or HCl in (1) is the mol weight, that is, one mol of NaOH is equivalent to one mol of HCl. In (2), two mols of NaOH are equivalent to one mol of H_2SO_4 , and the

2 The Standardization of Volumetric Solutions

equivalent weight of H_2SO_4 will be the molecular weight divided by 2, since the number of replaceable hydrogen atoms is 2, and a normal solution will contain this weight of H_2SO_4 in a liter of water. Equation (3) shows that 2 HCl are equivalent to 1 $\text{Ca}(\text{OH})_2$. Calcium hydroxide is dibasic, and therefore has the equivalent of two replaceable hydrogens. Hence, the equivalent reacting weight will be the molecular weight divided by two. In case (4), by inspection it will be seen that there will be three replaceable hydrogen atoms (if all are titrated) and that the equivalent reacting weight will be the molecular weight divided by three.

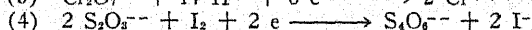
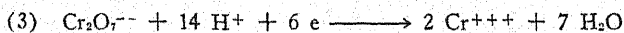
In dealing with oxidation-reduction equations, the reacting weight (or equivalent weight) of a substance is the weight of substance equivalent to one half mol of oxygen (one half mol of oxygen is equivalent to one mol of hydrogen). Since oxidation-reduction is really electron transfer, it is simpler to determine the change of valence from the equation involved. The molecular weight divided by the change in valence is the equivalent reacting weight, and this weight made up to one liter is equivalent to one gram atom of hydrogen, or one half gram atom of oxygen.

This may be illustrated more clearly, perhaps, by the following examples:



In the first equation, manganese, as a permanganate, with a valence of 7, has been reduced to a manganous salt having a valence of 2, or, in other words, there has been a transfer of 5 electrons. This reaction takes place in acid solution and the equivalent weight, therefore, is $\frac{\text{MnO}_4^-}{5}$.

Equation (2) represents oxidation with alkaline permanganate, and by inspection it is found that the valence change is 3. Consequently, there has been an electron transfer of 3, and the equivalent weight is $\frac{\text{MnO}_4^-}{3}$.



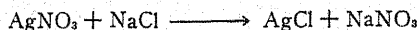
Example (3) illustrates dichromate oxidation, which involves a transfer of 6 electrons, and gives a reacting weight equal to $\frac{\text{Cr}_2\text{O}_7^{--}}{6}$. In the last equation (4), the iodine has been reduced from zero valence to a valence of minus 1, and therefore, the equivalent weight will be $\frac{\text{I}}{1}$.

Since oxidation is the result of a loss of electrons, and reduction represents a gain of electrons, it is not necessarily true that an oxidizing agent always contains oxygen [as for instance iodine in equation (4)]. Equations (1) and (2) show that the equivalent reacting weight of an oxidizing agent may vary depending upon the medium in which the reaction takes place.

The equivalent weights of precipitation reagents may

4 The Standardization of Volumetric Solutions

be likewise determined from their reactions. For instance :



By inspection, it is seen that one mol of silver nitrate reacts with one mol of sodium chloride to form one mol of silver chloride. Therefore, their equivalent reacting weights in this case are their molecular weights.

Standard solutions, in some cases, may be prepared without further standardization where the substance is known to be pure, and does not change appreciably due to atmospheric conditions. Potassium dichromate, potassium iodate, oxalic acid, and silver nitrate are a few examples. However, it is always desirable to standardize a solution. It is good practice to weigh the substance as accurately as possible, to avoid the necessity later of diluting to the proper normality. Also, it is advisable to weigh slightly more than the theoretical amount, since it is easier to dilute than to raise to the desired normality. The dilution may be calculated as follows (contraction of the solution being neglected, as usually no great error is involved) :

Let V = volume of solution before dilution
 V_1 = volume of solution after dilution
 N = normality of solution before dilution
 N_1 = normality desired after dilution

Then $NV = N_1V_1$

$$\text{or } V_1 = \frac{NV}{N_1}$$

and $V_1 - V = x$ cc of solvent to be added to the original volume.

Solutions as dilute as tenth normal are affected but little by temperature changes,^{1, 2, 3} but with half normal and normal solutions, the temperature should be considered. The following table, after W. Schloesser,² gives a partial list of corrections to be applied to standard solutions referred to 20° C as a standard temperature.

T°C	Water 0.01N Solutions 0.1N HCl	0.1N Solu- tions	0.5N HCl	1.0N HCl	0.5N NaOH	1.0N NaOH
15	+0.8	+0.9	+0.9	+1.0	+1.1	+1.3
16	0.6	0.7	0.8	0.8	0.9	1.1
17	0.5	0.6	0.6	0.6	0.7	0.8
18	0.3	0.4	0.4	0.4	0.5	0.6
19	0.2	0.2	0.2	0.2	0.2	0.3
20	0.0	0.0	0.0	0.0	0.0	0.0
21	-0.2	-0.2	-0.2	-0.2	-0.2	-0.3
22	0.4	0.4	0.4	0.5	0.5	0.6
23	0.6	0.6	0.7	0.7	0.8	0.9
24	0.8	0.9	0.9	1.0	1.0	1.2
25	1.0	1.1	1.1	1.2	1.3	1.5

Schloesser assumes the coefficient of cubical expansion of glass to be 0.000027.

Certain precautions should be observed regarding standard solutions. It is good policy to store all standard solutions in the dark, where there is a minimum of temperature variation, and where the containers cannot be contaminated with dust or organic material. Solutions should be labelled in the following manner :

¹ Yokichi Osaka, *J. Tokyo Chem. Soc.* **40**, 424 (1919); *Chemical Abstracts* **14**, 159 (1920).

² W. Schloesser, *Chem. Ztg.* **29**, 510 (1905).

³ N. Schoorl, *Chem. Weekblad* **23**, 581 (1926).

6 *The Standardization of Volumetric Solutions*

Name and formula

Normality or factor

Name and notebook reference of the person
making up and standardizing the solution

Temperature of standardization

Date of standardization

This information makes it easier to check any possible errors in standardization. It is also advisable to record the equivalent weight, to facilitate preparation of subsequent solutions. Solutions that have stood for a considerable time,⁴ and particularly those that show a tendency to deteriorate quickly, should always be re-standardized before using.

Usually, in the preparation of standard solutions, the theoretical amount of substance is weighed in air against brass weights, neglecting the effect of buoyancy. Since atomic weights and, it follows, molecular weights are calculated to vacuo, there is, therefore, an error introduced when weighings are made in air. The magnitude of this error is such that it may be neglected. The equivalent weights found in the following pages are not corrected to vacuo.

Archimedes' principle states that bodies immersed in a fluid are buoyed up by a force equal to the weight of the displaced fluid. This law holds for gases as well as for liquids.

⁴ J. Linder, *Mikrochemie*, Festschr. von Hans Molisch, 301-13 (1936).

If a mass of brass is weighed against brass weights, the buoyancy force on both sides of the balance is the same, provided the volume is the same, and no correction need be made. If, however, the density of the weights is greater than that of the substance being weighed, the apparent weight of the substance in air will be less than its true weight in vacuo. The weight reduced to vacuo may be calculated from the following formula:

$$w = W + W\delta \left(\frac{1}{d} - \frac{1}{d_1} \right)$$

where W = true weight

w = apparent weight in air

δ = density of air

d = density of substance being weighed

d_1 = density of weights used

Density of brass is 8.4, and density of air is 0.0012.

Since the majority of commonly used standard solutions cannot be prepared by direct weighing of the substance in question, some means must be taken to establish the exact value of the solution. Any errors in standardization will be recurrent in all subsequent determinations made with the solution. In the first place, therefore, some substance of known purity must be available for evaluating the solution. Certain requirements are necessary for a primary standard. It should have a high equivalent weight, be easily obtainable pure, or easily purified. It should be neither hygroscopic nor efflorescent.

8 *The Standardization of Volumetric Solutions*

It is obvious that the primary substance must bear a stoichiometrical relation to the standard solution.

In the actual standardization, several other points must be observed. In weighing out the primary standard, it must be remembered that, in general, the accuracy of an analytical balance is ± 0.1 mg, so that sufficient sample must be weighed to reduce this error to a minimum. This, in effect, is an argument for the use of substances having a high equivalent weight. The actual titration should fall within the limits of the burette, that is, it should not titrate over 50 cc. No less than 40 cc should be used. The errors involved in titration, while small, are cumulative, (reading, drainage, and error in the end point—plus or minus one drop). If the end point is overrun, say, by one drop, then the error involved here is about ± 0.03 cc, since this is approximately the volume of one drop from a fine-tipped burette. If, now, the remaining errors of reading and drainage are added to this, it is easily seen that at least 40 cc must be used in order to keep the errors within 0.1–0.2 per cent. Since the accuracy of standardization is between 0.1 and 0.2 per cent, it will be understandable that every precaution must be taken. Standardizations, involving a back titration with another standard solution, are open to further errors which may be additive, since they involve an additional titration. At least three checks should be made on any standardization. They should check within 0.2 per cent. Care-

fulness cannot be too highly stressed in the standardization of a reagent, since the accuracy of future determinations depends upon the accuracy with which the value of the standard solution was determined.

The calculations involved in volumetric standardizations are very simple. Normality may be calculated according to the following formula.

$$\text{Normality} = \frac{\text{weight of standard substance}}{\text{milliequivalent of std.} \times \text{cc titration}}$$

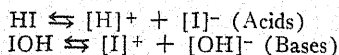
The milliequivalent may be defined as the weight of standard substance contained in one cubic centimeter of a normal solution of that standard substance. The milliequivalent multiplied by the number of cubic centimeters used for titration gives the weight in grams of standard substance. The weight of standard substance divided by this gives the ratio of the standard solution to the theoretical normal solution. In other words, if the normality found is 0.1050 normal, it means simply that one cubic centimeter of the solution contains 1.050 times as much as the theoretical amount.

In the choice of a suitable indicator, the field is so large that it may, in many cases, be left to the discretion of the operator. There are, however, certain requirements to be met, namely, an indicator whose transition range is within the range of the reaction involved, and a color change which is sharp enough to be differentiated by the analyst.

10 The Standardization of Volumetric Solutions

The point at which the indicator changes color is taken as the end point, meaning that at this point, an equivalent amount of standard reagent has been added. Strictly speaking, this may or may not be the exact end point or equivalence point. This can be determined by electrometric titration, the difference in the two titrations being known as the titration error.

Most indicators are organic, and are either weak acids or weak bases. They are slightly ionized, according to the following:



Oxidation and reduction indicators depend for their color changes on oxidation or reduction of themselves. In some cases, the reagent itself acts as its own indicator.

A recent class of indicators, known as adsorption indicators,⁵ has been used with more or less success in the determination of halides and sulphates. In general, they are not applicable to standardizations, although they have been used⁶ in acidimetry and alkalimetry. A theoretical discussion of various types of indicators will be found in Kolthoff and Furman, *Volumetric Analysis*, Vol. I (1928), 82.

⁵ A. R. Ubbelohde, *Chem. Rev.* 16, 53 (1935).

⁶ Sachindra Nath Roy, *J. Indian Chem. Soc.* 14, 120 (1937); see also *Chemical Abstracts* 31, 5293 (1937); *Chemical Abstracts* 30, 8064 (1936).

CHAPTER II

Calibration of Volumetric Apparatus

SINCE volumetric procedures require accurate measurement of volume, the importance of knowing the exact volumes of the various apparatus used cannot be overlooked. The simplest and most obvious solution to this problem, wherever possible, is to use apparatus calibrated by the U. S. Bureau of Standards. Apparatus calibrated by the Bureau is always accompanied by a table of volume corrections over a range of working temperatures. This, however, is comparatively expensive, and it is easy enough to purchase a good grade of glassware that falls within the limits of tolerance allowed by the Bureau of Standards, and calibrate it in the laboratory. It is never advisable to rely on the accuracy of a piece of apparatus without first calibrating it.¹

In the process of standardization, volumetric flasks, pipettes, and burettes are necessary. Volumetric flasks are graduated to *contain* a definite volume, and pipettes

¹ *Bur. Standards Circ. No. 9* (1916).

12 *The Standardization of Volumetric Solutions*

and burettes to *deliver* a definite volume. Before any attempt is made to calibrate apparatus, it must be thoroughly cleaned. This is done by rinsing with tap water, filling with fresh chromic acid, and letting stand for several hours. After this treatment, the chromic acid is withdrawn, and the apparatus washed free from the acid with tap water. It is now washed with distilled water and drained. If the water does not appear to wet the inside of the apparatus evenly, several washes with acetone, and then distilled water may be efficacious. If this does not have any effect, another treatment with chromic acid will be necessary.

Since the calibration is made with water, it is not necessary to dry the apparatus. All volumetric apparatus are calibrated to contain or deliver a definite volume at a standard temperature, usually taken at 20° C. This means, of course, that at this temperature, the apparatus will contain the designated volume. At any other temperature, the volume will vary depending upon the expansion of the glass and the density of water. Buoyancy effect is also taken into consideration, using 0.0012 gm per cc, the density of air (not strictly correct, because this figure will vary slightly depending upon temperature, humidity and pressure), as sufficiently accurate for all calibrations.

Usually, the temperature at the time of calibration is not 20° C, so that all weighings are made under existing conditions and referred back to 20° C. The

liter is the unit of volume in the metric system, and is the volume of a mass of one kilogram of water at maximum density.

CALIBRATION OF FLASKS

Fill the flask to the graduation on the neck with distilled water at room temperature and weigh. This weight is reduced to vacuo (mass), according to the formula:

$$w = W + W\delta \left(\frac{1}{d} - \frac{1}{d_1} \right) \text{ (See Chapter I)}$$

The volume at room temperature is this mass divided by the density of water at room temperature.

$$\text{Volume at R. T.} = \frac{\text{Mass}}{d_{H_2O}}$$

This gives the volume of the flask at room temperature. It is now necessary to calculate this volume to 20° C, and this may be done by applying the following:

$$V_T = V_{T_1} + 0.000025 V_{T_1}(T - T_1)$$

Where V_T = Volume at standard temperature
 V_{T_1} = Volume at calibration temperature
 T = Standard Temperature
 T_1 = Calibration Temperature

Coefficient of cubical expansion of glass* = 0.000025

* Coefficient of cubical expansion of Pyrex glass is 0.00000032 or less, between 19 and 350° C.

14 *The Standardisation of Volumetric Solutions*

CALIBRATION OF PIPETTES

After cleaning the pipette, immerse the tip in water, fill to the mark, discard and fill again exactly to the graduation. Wipe any excess water from the pipette by means of a soft rag and transfer the contents to a tared and stoppered Erlenmeyer flask, allowing the pipette to remain vertical until discharged and then touching the tip to the side of the flask and allowing it to remain for fifteen seconds. Do not blow out the pipette. Reweigh the Erlenmeyer flask and calculate the volume in the same manner as for volumetric flasks.

CALIBRATION OF BURETTES

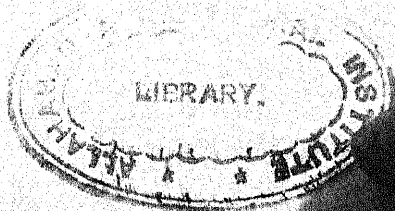
The calibration of a burette may be carried out in two ways: 1. Measure 5 cc of water from the burette into a tared and stoppered 100 cc Erlenmeyer flask and weigh. Record the weight. Add 5 cc more to the flask and reweigh. Repeat this process until the capacity of the burette has been measured into the flask and weighed. 2. Measure 5 cc from the burette and weigh. Refill the burette and measure 10 cc into a flask and weigh. Repeat this procedure until the last weighing represents the capacity of the burette. The calculations are the same as for flasks and pipettes. The difference between the true volume and the observed volume is the correction to be applied in a titration. A curve may

be plotted to show the correction and true volume at any point.

When reading the volume, care must be taken to avoid parallax. In the case of pipettes and flasks or any piece of apparatus on which the graduation extends around the circumference, this is avoided, but with burettes, a possible error may occur if the graduation and the eye are not in the same horizontal plane. The error may be either positive or negative. This may be overcome by using a strip of paper having a straight edge, bringing it to the bottom of the meniscus and lining up both sides.

The method of calibration herein described is probably the most common one. Another means of calibration is by the use of Morse-Blalock² bulbs, which, however, require a more complicated set-up, and are generally not available in most analytical laboratories.

² Morse and Blalock, *Am. Chem. J.* 16, 479 (1894).



CHAPTER III

Indicators: *Definition, Classification, Classification of Reaction, Acid-Base Indicators, Oxidation-Reduction Indicators, Indicators for Precipitation Reactions. General Discussion.*

ANY compound in solution exhibiting a color change or producing a precipitate, by addition of an excess of one of the reactants, may be considered as an indicator. In other words, an indicator produces a visual change at, or near, the equivalence point. It may be a separate compound or one of the reagents, as in the case of permanganate or iodine.

Indicators may be divided roughly into three classes:

1. acid-base
2. oxidation-reduction
3. precipitation

For an extended survey of indicators, and theoretical considerations, reference should be made to the many excellent books on this subject.^{1, 2, 3, 4}

¹ Kolthoff and Furman, *Indicators* (Wiley).

² Kolthoff and Furman, *Volumetric Analysis, Vol. I & II* (Wiley, 1929).

³ Clark, *Determination of Hydrogen Ions* (Williams & Wilkins).

⁴ Hubert T. S. Britton, *Hydrogen Ions* (Van Nostrand).

ACID-BASE INDICATORS

The color change exhibited by indicators is produced by a change in H^+ concentration, and the range through which this occurs is called the transition interval. Most acid-base indicators are weak organic acids or bases which give one color when undissociated (pseudo form) and another when ionized (ionogen). Since they are weak acids or bases, the mass action law applies, and it is obvious, therefore, that the indicator change is a function of the H^+ concentration.

Thus, if $HI \rightleftharpoons [H^+] + [I^-]$

$$\text{then, } K_{\text{Ind.}} = \frac{[H^+] \times [I^-]}{HI}$$

Transposing, $K_{\text{Ind.}} \times HI = [H^+] \times [I^-]$

$$\text{or } \frac{K_{\text{Ind.}}}{[H^+]} = \frac{[I^-]}{HI}, \text{ so that when}$$

$$K_{\text{Ind.}} = [H^+], [I^-] = HI,$$

and the indicator is half changed over. At any pH, then, the equilibrium constant holds, and at any particular instant, there are present both acid and basic phases. At some point, however, either one will be in sufficient concentration to cause a visual change of color.

This change, for the most part, is not sudden, but covers from one to several pH units. This is due,

18 *The Standardization of Volumetric Solutions*

mainly, to the inability of the eye to gauge the color change accurately.

The transition range, obviously, has an upper and lower limit, at one end of which, the acid form predominates, whereas the other is alkaline.

If, for instance, 10% of the alkaline form of an indicator is sufficient to produce a visible change in the presence of the acid form, then,

$$\frac{K_{\text{Ind.}}}{[\text{H}^+]} = \frac{[\text{I}^-]}{\text{HI}} = \frac{1}{10}, \text{ and}$$
$$[\text{H}^+] = K_{\text{Ind.}} \times 10$$

Expressing this as a logarithmic function,

$$\text{pH} = \text{p}K_{\text{Ind.}} + 1$$

Now, conversely, if it is assumed that 10% of the acid form is enough to cause a color change in the presence of 90% of the alkaline form, then,

$$\frac{K_{\text{Ind.}}}{[\text{H}^+]} = \frac{[\text{I}^-]}{\text{HI}} = \frac{10}{1}$$

or $[\text{H}^+] = \frac{K_{\text{Ind.}}}{10}$

or $\text{pH} = \text{p}K_{\text{Ind.}} - 1$

The transition interval, therefore, is equivalent to 2 pH units.

The majority of indicators is affected by any great

change in temperature. Salt error, however, may be neglected, unless the concentration is very high. It tends to affect the equilibrium and the color change of the indicator, due to the difference in absorption of light.

A large variety of indicators is available for acid-base titrations, and a suitable choice is dependent upon the classification of the reaction, that is:

1. strong acid-strong base
2. weak acid-strong base
3. strong acid-weak base
4. weak acid-weak base

Each case will be considered separately.

1. Strong acid-strong base. In this case, it may be assumed that both are completely ionized, and if the base is as strongly ionized as the acid, complete neutrality is indicated. Since the definition of a neutral solution is one in which the $[H^+]$ and $[OH^-]$ concentrations are both 10^{-7} , then for this type of neutralization, an indicator having a transition range around pH 7 is acceptable.

2. Weak acid-strong base. If an acid is less strongly ionized than the base used in the titration, equilibrium will be attained in a basic solution. This conclusion is obvious, when it is realized that two conditions must be fulfilled: first, that the ionization constant of the acid must be satisfied, and second, that $C_H \times C_{OH} = 10^{-14}$ (actually 1.2×10^{-14}) will be maintained. At equilib-

20 *The Standardization of Volumetric Solutions*

rium, there must be unionized acid present. This lowers the concentration of $[H^+]$ and leaves free $[OH^-]$ in the solution. The pH of the solution, at equilibrium, will be greater than 7, hence, an indicator having a range greater than pH 7 must be used.

3. Strong acid-weak base. If the conditions stated under 2 are reversed, it will be seen that equilibrium will take place in acid solution. In this case, an indicator having a pH of less than 7 should be used.

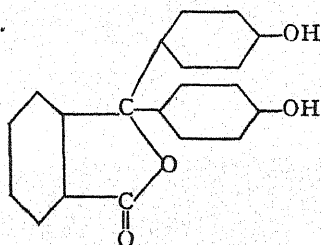
4. Weak acid-weak base. In this case, three equilibrium constants must be satisfied, namely, ionization constants of both acid and base, and ionization constant of the water formed by the reaction. If the acid and base are ionized to about the same degree, e.g. acetic acid and ammonia, then the resulting solution will have a pH of 7. If one is more strongly ionized than the other, the same conditions will exist as stated previously in cases 2 and 3, and the same kind of indicators chosen.

The following represent a few of the indicators most commonly used in acid-base reactions. They cover a wide range of pH.

Phenolphthalein

Type: Belongs to the phthalein group.

Structural formula:

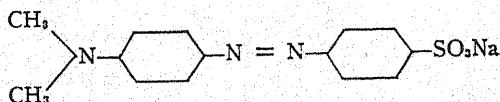


pH range 8.3–10.0. Color change from colorless to red violet.

Methyl Orange (sodium dimethylamino azobenzene sulphonate)

Type: Belongs to the azo group.

Structural formula :



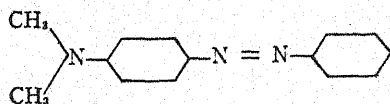
pH range 2.9–4.5. Color change from orange red to orange yellow. Although this indicator is widely used, the color change is not as sharp as could be desired, and it may be replaced, for instance, by methyl yellow. The color change for this indicator is much sharper. Methyl orange is not affected by carbon dioxide.

Methyl Yellow (dimethylamino azobenzene)

Type: Belongs to the azo group.

Structural formula :

22 The Standardization of Volumetric Solutions

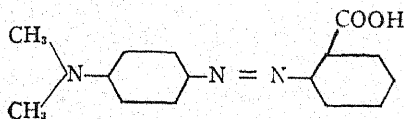


pH range 2.9–4.0. Color change from red to yellow.
(Not affected by CO_2).

Methyl Red (dimethylamino azobenzoic acid)

Type: Belongs to the azo group.

Structural formula :

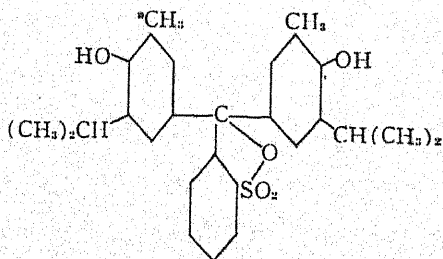


pH range 4.2–6.3. Color change from red to yellow.

Thymol Blue (thymol sulphon phthalein)

Type: Belongs to the phthalein group.

Structural formula :



pH range: Acid 1.2–2.8
alkaline 8.0–9.6.

Color change in the acid range from red to yellow, and yellow to blue in the alkaline range.

OXIDATION-REDUCTION INDICATORS

Any system in which there is a change of valence may be classified as an oxidation-reduction reaction. Therefore, when an atom or complex ion is oxidized, its positive valence is increased, or its negative valence is decreased, and the converse is also true of reduction. In other words, a substance which is oxidized gives up electrons, and a substance which is reduced adds electrons.

Previously, the use of outside indicators was more or less universal for determining the end point. If colorless solutions are to be titrated, it is possible for the reagent to act as its own indicator, for instance, potassium permanganate, ceric sulphate, and iodine.

Internal oxidation-reduction indicators have been applied to dichromate, permanganate, ceric sulphate, and ferrocyanide titrations. An oxidation-reduction indicator should, of course, be reversible, otherwise its use is limited. For every oxidation-reduction equation, there can be calculated a definite electrode potential using the Nernst equation.⁵

$$E = \frac{RT}{nF} \ln \frac{p}{P},$$

⁵ Engelder, *Calculations of Qualitative Analysis*, Chapter IX, p. 131.

24 The Standardization of Volumetric Solutions

which can be simplified to

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

or

$$E = \frac{0.059}{n} \log C + \frac{0.059}{n} \log \frac{1}{k}$$

If the concentration is one molar, then

$$E = \frac{0.059}{n} \log \frac{1}{k}$$

or

$$E = E_0$$

E_0 is the oxidation potential at molar concentration and is a constant for each system, so that the oxidation potential may be calculated for any mixture, from the following equation:

$$E = E_0 + \frac{0.059}{n} \log \frac{C_{\text{oxd}}}{C_{\text{red}}}$$

where C_{oxd} is the concentration of the oxidized ion, and C_{red} , the concentration of the ion in reduced form.

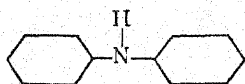
The selection of a suitable indicator is based on the normal potentials of both indicator and the oxidizing-reducing system in question, since the specific action of the indicator is dependent upon its electrode potential. Therefore, any indicator, having a lower oxidation potential than the system in which it is used, will exhibit a color change. There must not, however, be a very

large difference. If this is the case, the oxidation potential (of the system) should be reduced, and this is accomplished in some cases by forming complex ions.

The following indicators have been used successfully in oxidation-reduction reactions.

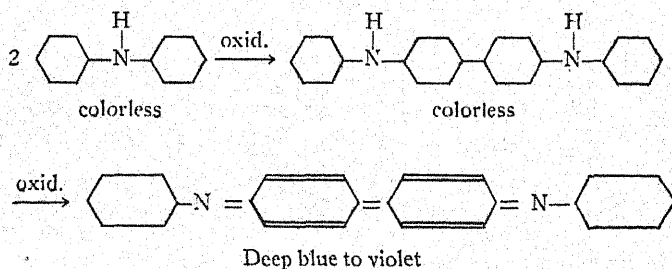
Diphenylamine

Structural formula:



Oxidation potential: -0.76 volts.

The first step in the oxidation of this indicator is to diphenylbenzidine, and thence to colored compound



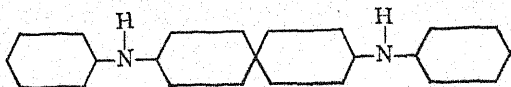
Color change is colorless to deep blue or violet. Since some of the reagent goes to complete the oxidation of the indicator, it is necessary to make a correction ⁶ for the amount used.

⁶ W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* **49**, 356 (1927).

26 The Standardization of Volumetric Solutions

Diphenylbenzidine

Structural formula:



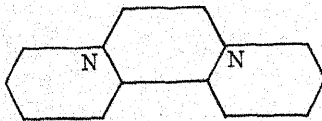
Oxidation potential: -0.76 volts.

Color change is from colorless to deep blue or violet.

The oxidation proceeds as above. The blue compound is stable for only a short while in the presence of oxidizing agents.

Ortho-Phenanthroline Complex⁷

Oxidation potential is -1.14 volts. The usual form of this indicator is the ferrous ion complex. The structural formula of *o*-phenanthroline is:



It dissolves in solutions of ferrous salts, three molecules combining with one ferrous ion.

Color change is from red to blue.

Starch Solution^{8, 9}

The preparation of starch solution is more difficult

⁷ *Ortho-phenanthroline*, monograph published by The G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio.

⁸ C. L. Alsberg and E. P. Griffing, *J. Am. Chem. Soc.* **53**, 1401 (1931).

⁹ C. L. Alsberg and E. P. Griffing, *J. Am. Chem. Soc.* **48**, 1299 (1926).

than is ordinarily supposed. A solution which will prove satisfactory over a long period can be prepared¹⁰ in the following manner: Mix 0.5 gm of potato starch with 2.5 cc of water and pour into 200 cc of boiling water, stirring meanwhile. Boil fifteen minutes. Cover the flask or beaker with a watch glass to prevent scum forming by evaporation during boiling. The final solution should not contain any suspended matter. If this is kept covered and allowed to stand on a steam plate, the solution will keep indefinitely. If heating is impossible, 0.25 gm of salicylic acid may be added as a preservative. With this addition, starch solutions have given good end points after a year, although considerable sediment had formed, and only the supernatant liquid was used.

The condition of starch, as received from supply houses, is somewhat uncertain. Sometimes fresh starch contains dextrin, which gives a reddish violet color, and is not immediately discharged by thiosulphate. Starch of this sort should be discarded. The color change is from colorless to blue. In the presence of iodide, the sensitivity is of the order of 2×10^{-5} concentration of iodine. Heat decreases the sensitivity, as does alcohol.

INDICATORS FOR PRECIPITATION REACTIONS

In precipitation reactions, application of the differences in solubility is made. To take a concrete example,

¹⁰ M. Starr Nichols, *J. Ind. Eng. Chem., Anal. Ed.* 1, 215 (1929).

28 The Standardization of Volumetric Solutions

the reason that potassium chromate can be used as an indicator in the standardization of silver nitrate with sodium chloride may be explained in the following manner: The solubility of silver chloride is extremely small and that of silver chromate relatively large, so that no silver chromate will be formed until all chloride ions have been precipitated. Ferric alum acts in a similar manner in the silver nitrate-ammonium thiocyanate reaction.

GENERAL DISCUSSION

The short list of indicators already described should in no way be taken as representative of indicators as a whole. They are discussed only from the standpoint of their usefulness in standardization of normal solutions. Some indicators such as thymol blue and 4-nitrocatechol¹¹ exhibit three color changes, representing two transition intervals, one in the acid range, and one in the alkaline. Often, two indicators are mixed^{12, 13, 14} to give a transition range between certain pH values.

New oxidation-reduction indicators are constantly being prepared and tested. It has been found that the

¹¹ S. R. Cooper and V. J. Tulane, *J. Ind. Eng. Chem., Anal. Ed* **8**, 210 (1936).

¹² H. A. J. Pieters, *Chem. Weekblad* **32**, 539.

¹³ Kurt Hoppner, *Deut. Zuckerind.* **61**, 361 (1936).

¹⁴ Kolthoff and Furman, *Volumetric Analysis, Vol. II* (1929), p. 64.

sodium or barium salt of diphenylamine sulphonie acid¹⁵ is a suitable oxidation-reduction indicator, particularly in presence of tungstates. In this respect, it is better than either diphenylamine or diphenylbenzidine, since tungstates interfere with these indicators.

Phenylanthranilic acid,^{16, 17} para and meta tolylphenylamine, and naphthidine¹⁸ have been proposed and used.

There is little to be said regarding adsorption indicators, as they are seldom used in procedures for standardizations. Fluorescein and eosin have been known and used for some time in the determination of halogens as the silver halides. Sodium rhodizionate^{19, 20} (sodium salt of tetrahydroxy quinone) is being used as an internal indicator for the determination of sulphates volumetrically. In the use of these indicators, there is a tendency toward an indicator lag, particularly in solutions of fairly high concentrations.

¹⁵ L. A. Sarver and I. M. Kolthoff, *J. Am. Chem. Soc.* **53**, 2902, 2906 (1931).

¹⁶ A. U. Kirsanov and U. M. Cherkasov, *Zavodskaya Lab.* **5**, 143; *Bull. Soc. Chim. (5)*, **3**, 817.

¹⁷ V. S. Svirokomskii and V. V. Stepin, *J. Am. Chem. Soc.* **58**, 928 (1936).

¹⁸ Leora E. Straka with R. E. Oesper, *J. Ind. Eng. Chem., Anal. Ed.* **6**, 465 (1934).

¹⁹ Mutschin and Pollak, *Z. Anal. Chem.* **108**, 8 (1937).

²⁰ Mutschin and Pollak, *Z. Anal. Chem.* **108**, 309 (1937).

SUPPLEMENTARY REFERENCES

A Symposium on Indicators, *Chemical Reviews* **16**, 53 (1935).

Advances in Indicators for Use in Volumetric Analysis, A. E. Jennings, Jr., *Can. Chem. Met.* **20**, 220 (1935).

Chromotropic Acid as an Indicator in Fluorescence—Volumetric Analysis, Kocsis and Nagy, *Z. Anal. Chem.* **108**, 317 (1937).

Indicators, I. M. Kolthoff, *J. Ind. Eng. Chem., Anal. Ed.* **8**, 237 (1936).

Diphenylcarbazine, An Internal Indicator for Use in the Titration of Iron with Dichromate, H. E. Crossley, *Analyst*, **61**, 164.

Internal Indicator for Dichromate-Titration of Iron, M. E. Weeks, *J. Ind. Eng. Chem., Anal. Ed.* **4**, 127 (1932).

Oxidation-Reduction Indicators for Use with Dichromate II, Stuart Cohen and Ralph E. Oesper, *J. Ind. Eng. Chem., Anal. Ed.* **8**, 364 (1936).

A Better Titrating Solution Using Diphenylamine Indicator, W. K. Gibson, *Chemist-Analyst* **26**, 28 (1937).

Indicator: Ferrous-ortho-phenanthroline, Walden, Hammet, and Chapman, *J. Am. Chem. Soc.* **53**, 3908 (1931).

Starch Indicator, Fales, *Inorganic Quantitative Analysis* (The Century Co., New York, 1925), 300.

The Constitution of Starch Iodide, A. Lottermoser, *Z. Angew. Chem.* **34**, Aufsatzteil, 427 (1921); *Chemical Abstracts* **16**, 10 (1922).

The Taking Up of Iodine by Various Substances, A. Lottermoser, *Kolloid Z.* **33**, 271 (1923); *Chemical Abstracts* **18**, 925 (1924).

Starch Iodide, A. Lottermoser, *Z. Angew. Chem.* **37**, 84 (1924); *Chemical Abstracts* **18**, 950 (1924).

CHAPTER IV

Standard Substances

IF THE concentration of a solution is to be determined accurately, it is necessary to compare it with some substance of known purity. Not all substances are suitable for standards, and, because of this fact, certain requirements are necessary, chief among which are high equivalent weight, stability at ordinary temperatures, ease of purification, solubility and absence of side reactions. The substance should neither deliquesce nor effloresce.

Many attempts have been made to prepare a universal primary standard, but, so far, such work has not been successful. There are, however, many excellent primary standards available. Some of these overlap, that is to say, they may be used as a standard for more than one type of standard reaction. They may be placed in general classifications as follows:

1. Standard substances for acids and bases
2. Standard substances for precipitation reagents
3. Standard substances for oxidation-reduction reagents

32 The Standardization of Volumetric Solutions

Considering the first class of standards, they may be further subdivided into those suitable for acids and those suitable for bases. In the first category falls anhydrous sodium carbonate, the classical primary standard for acids. In spite of the recognized shortcomings, it has stood the test of time. Extreme care, however, must be exercised in using it, both in preparation and in standardization. Smith and Croad¹ have found that it is not safe to heat the bicarbonate above 300° C in preparing the carbonate, as there is appreciable decomposition at 310–315° C. Sodium carbonate suitable for standardization purposes, according to Stalony-Dobrzanski,² is obtained by heating sodium bicarbonate between 150 and 280° C. Decomposition of the sodium bicarbonate is completed after 100 minutes. There is also a disadvantage of low equivalent weight and the fact that it is hygroscopic.

Borax, originally used in the anhydrous state, was unsatisfactory due to the difficulty in preparing and keeping the anhydrous salt. The decahydrate,^{3, 4, 5} how-

¹ G. F. Smith and G. F. Croad, *Ind. Eng. Chem., Anal. Ed.* **9**, 141 (1937).

² J. Stalony-Dobrzanski, *Roczniki Chem.* **14**, 1106 (1934).

³ G. Kilde, *Dansk. Tids. Farm.* **10**, 273 (1936), (English summary).

⁴ F. H. Hurley, Jr., *Ind. Eng. Chem., Anal. Ed.* **8**, 220 (1936).

⁵ F. H. Hurley, Jr., *Ind. Eng. Chem., Anal. Ed.* **9**, 237 (1937).

ever, makes a suitable standard which possesses the advantage of a high equivalent weight.

Carlton⁶ proposed the use of symmetrical diphenyl guanidine, but a comparison made by Thornton and Christ⁷ showed that the results obtained were low and suggested that a better method of purification was necessary if it was to be used as a standard. On the other hand, Young⁸ states that it may be purified simply by recrystallization to provide a satisfactory primary standard. Guanidine carbonate,⁹ prepared from calcium cyanide, is very pure, contains no water of crystallization, and is not hygroscopic. It behaves as a monoacidic base and is accurate enough for use as a standard in routine work.

Potassium bicarbonate,^{10, 11, 12, 13} as an acidimetric standard, is prepared by passing CO₂ into an alcoholic solution of potassium hydroxide. It is a reliable standard for all but very accurate work. Solutions stronger than N/10 show a tendency to evolve CO₂.

⁶ C. A. Carlton, *J. Am. Chem. Soc.* **44**, 1469 (1922).

⁷ W. M. Thornton and C. L. Christ, *Ind. Eng. Chem., Anal. Ed.* **9**, 339 (1937).

⁸ J. W. Young, *Can. J. Research* **17B**, 192 (1939).

⁹ A. H. Dodd, *J. Soc. Chem. Ind.* **40**, 80-90 T (1921).

¹⁰ L. W. Winkler, *Z. angew. Chem.* **28**, 264 (1915); *Chemical Abstracts* **9**, 2747 (1915).

¹¹ G. Incze, *Z. anal. Chem.* **54**, 585 (1916).

¹² G. Bruhns, *Chem. Ztg.* **41**, 386 (1917); *J. Chem. Soc.* **112**, II, 419.

¹³ G. Bruhns, *Chem. Ztg.* **48**, 89 (1924).

34 The Standardization of Volumetric Solutions

Dipotassium periodate,¹⁴ $K_2H_3IO_6 \cdot 3H_2O$, reacts quantitatively with strong acids in the following manner:



It has the advantage of a relatively high equivalent weight. A sharp end point is obtained with methyl red as an indicator.

The use of thallous carbonate has been suggested by Hac and Kamen.¹⁵ As a result of their experiments, they concluded that it was a satisfactory primary standard. Reproducible results, using methyl orange as an indicator, were obtained, which agreed within a few thousandths of 1%, and the values compared favorably to those resulting from the use of Na_2CO_3 , $Na_2B_4O_7$ and $Na_2C_2O_4$. Work by Berry,¹⁶ and Jensen and Nilssen¹⁷ gives further proof of the suitability of thallous carbonate.

A method of great precision for the standardization of hydrochloric acid is the use of metallic silver¹⁸ as

¹⁴ L. Malaprade, *Congr. chim. ind., Compt. rend.* 18 ème Congr. Nancy Sept.-Oct. (1938), 91.

¹⁵ R. Hac and K. Kamen, *Collection Czechoslov. Chem. Commun.* 4, 145; *Chem. Listy* 26, 6 (1932); *Chemical Abstracts* 26, 3746 (1932).

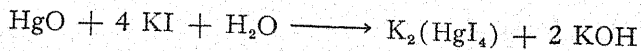
¹⁶ A. J. Berry, *Analyst*, 64, 27 (1939).

¹⁷ Einar Jensen and Bailli Nilssen, *Ind. Eng. Chem., Anal. Ed.* 11, 508 (1939).

¹⁸ C. W. Foulk and L. A. Pappenhagen, *Ind. Eng. Chem., Anal. Ed.* 6, 430 (1934).

an ultimate standard. It is a useful nephelometric method, and the results obtained exceed those of other methods in accuracy.

Another substance obtainable in a high degree of purity is yellow mercuric oxide.^{19, 20} It is not hygroscopic and contains no water of crystallization. The principle depends upon the following reaction:



The mercuric oxide is dissolved in a large excess of potassium iodide (0.5 gm HgO and 7.5 gm KI), and the resulting potassium hydroxide is titrated with the acid to be standardized, using phenolphthalein as an indicator. Kolthoff and van Berk²¹ observe that whereas results by this method are accurate to within 0.1%, the method is not as precise as standardization with borax. Lazarkevich²² confirms this and states that mercuric oxide should be used only for rough work.

A report by Vandaveer²³ on the standardization of acidimetric solutions compares the results obtained by

¹⁹ L. Rosenthaler and A. Abelman, *Pharm. J.* 91, 144, 186; *Chemical Abstracts* 7, 3726 (1913).

²⁰ G. Incze, *Z. anal. Chem.* 56, 177 (1917); *J. Soc. Chem. Ind.* 36, 671 (1917).

²¹ I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.* 71, 339 (1927).

²² N. A. Lazarkevich, *Ukrainskii Khim. Zhur.* 4, Sci. Pt. 405 (1929); *Chemical Abstracts* 24, 3456 (1930).

²³ R. L. Vandaveer, *J. Assoc. Official Agri. Chem.* 22, 563 (1939).



36 *The Standardization of Volumetric Solutions*

standardizing 0.1N HCl with borax, sodium carbonate, and by precipitation as silver chloride. Considerable merit is claimed for borax and carbonate, but the results by silver chloride precipitation are not satisfactory, due, primarily, to the solubility of silver chloride. *

Bromocyanogen ²⁴ has been proposed as a universal standard for acids, silver nitrate, and sodium thiosulphate. It is, however, a disagreeable compound to work with, and its use is limited.

The standardization of bases by titration with a previously standardized acid is suitable for control work, but is affected, naturally, by those errors occurring in the initial standardization. It is necessary, therefore, to apply the same procedure to bases as was used for acids, namely, titration by means of a primary standard.

An early attempt to establish a universal standard was the use of ammonium triiodate, $(\text{NH}_4)\text{H}_2(\text{IO}_3)_3$.²⁵ It was prepared by the action of ammonium chloride on iodic acid, allowing the solution to stand 24–48 hours, and recrystallizing the salt from hot water. It contains no water of crystallization and can be dried over sulphuric acid. Borax ²⁶ may be used for strong bases. Boric acid is very weak and can be titrated only in fairly high concentrations using a reference solution. It does, however, form compounds with polyhydric alco-

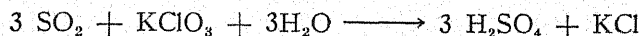
²⁴ M. Moller, *Z. anal. Chem.* **99**, 351 (1934).

²⁵ E. Riegler, *Bull. assoc. chim. suc. dist.* **24**, 528; *Chemical Abstracts* **1**, 705 (1907).

²⁶ M. G. Mellon and V. N. Morris, *Ind. Eng. Chem.* **17**, 145 (1925).

hols, giving strong complex acids which give a sharp end point with phenolphthalein. Glycerine (neutral), glucose, or mannitol may be used. Mannitol is very satisfactory, but when glycerine is used, there is an indicator lag.

The use of potassium chlorate as a standard for alkali has been suggested by van Valkenburg.²⁷ A solution of the salt (approximately normal) is boiled and reduced, while boiling, with SO₂ according to the equation:



The excess SO₂ is boiled off, and the acid titrated with alkali, using phenolphthalein as an indicator.

Potassium binoxalate,²⁸ and either potassium or sodium acid phthalate²⁹ are suitable standards, the phthalates, in particular, because of their high equivalent weights.

Ashley and Hulett³⁰ proposed the use of cadmium sulphate as a standard for alkali. They allowed a solution of the salt to evaporate spontaneously and separated the clear crystals. From a given weight of the clear crystals, a known quantity of sulphuric acid

²⁷ H. B. van Valkenburg, *J. Am. Chem. Soc.* **42**, 757 (1920).

²⁸ Yukichi Osaka and Kinji Ando, *J. Tokyo Chem. Soc.* **41**, 945 (1920); *Chemical Abstracts* **15**, 1472 (1920).

²⁹ W. S. Hendrixson, *J. Am. Chem. Soc.* **37**, 2352 (1915).

³⁰ S. E. Q. Ashley and G. A. Hulett, *J. Am. Chem. Soc.* **56**, 1275 (1934).

38 *The Standardization of Volumetric Solutions*

was obtained by dissolving the sulphate in water and depositing the cadmium on a mercury cathode. The results agreed with values obtained using benzoic acid, potassium acid phthalate, and constant-boiling hydrochloric acid.

By far the largest class of compounds available for the standardization of bases is the organic acids. Their solubility in water is usually low and they are, for the most part, dissolved and titrated in an alcohol-water mixture.

Phelps and Weed³¹ examined a number of organic compounds, namely, succinic acid, succinic anhydride, malonic acid, benzoic acid, phthalic acid, and phthalic anhydride and found excellent agreement. On the other hand, Peters and Sanchelli³² were unable to duplicate the work of Phelps and Hubbard³³ who had previously used succinic acid for standardizing ammonia. These authors obtained normalities which were high compared with those measured by other methods. Correct results, according to Ljunggren,³⁴ may be obtained with *N*/10 alkalis by dissolving succinic acid in a

³¹ I. K. Phelps and L. H. Weed, *Am. J. Sci.* 26, 138 (August).

³² C. A. Peters and V. Sanchelli, *Am. J. Sci.* 41, 244 (1916).

³³ I. K. Phelps and J. L. Hubbard, *Am. J. Sci.* 23, 211; *Z. anorg. Chem.* 53, 361; *Chemical Abstracts* 1, 1832 (1907).

³⁴ G. Ljunggren, *Svensk Kem. Tid.* 36, 25 (1923); *Chemical Abstracts* 18, 1447 (1924).

minimum quantity of CO₂-free water (no more than 10 cc), and using 3-4 drops of 1:1000 phenolphthalein solution as an indicator.

Adipic acid^{35, 36} and salicylic acid³⁷ are satisfactory standards, although the values obtained with the latter³⁸ are somewhat low. Furoic acid,³⁹ which possesses the advantage of being soluble in water, gives about the same accuracy as benzoic acid. Aminosulphonic acid⁴⁰ and the sulphuric acid salts of aromatic amines⁴¹ have also been used and are capable of reasonable accuracy.

Sulphamic acid, NH₂SO₃H,⁴² has been proposed as an alkalimetric standard. It is easily purified, is not hygroscopic, and is soluble in water. Aqueous solutions hydrolyze, on standing, to ammonium acid sulphate.

The standardization of silver nitrate solutions is accomplished either gravimetrically or volumetrically; the

³⁵ F. Th. van Voorst, *Chem. Weekblad*, **25**, 22 (1928).

³⁶ A. H. Meyling, *J. S. African Chem. Inst.* **18**, 23 (1935).

³⁷ J. Rosicky and J. Tamchyna, *Chem. Listy*, **25**, 468 (1931); *Chemical Abstracts* **26**, 4006 (1932).

³⁸ S. Skromovsky, *Collection Czechoslov. Chem. Communications* **5**, 143 (1933); *Chemical Abstracts* **27**, 3418 (1933).

³⁹ H. B. Kellog and Ada M. Kellog, *Ind. Eng. Chem., Anal. Ed.* **6**, 251 (1934).

⁴⁰ L. Herboth, *Arch. Phar.* **262**, 517 (1924).

⁴¹ E. Strasser, *Z. anal. Chem.* **82**, 114 (1930).

⁴² Sister M. Josetta Butler, G. F. Smith and L. F. Andrieth, *Ind. Eng. Chem., Anal. Ed.* **10**, 690 (1938).

40 *The Standardization of Volumetric Solutions*

former by precipitation of the silver as silver chloride with a slight excess of sodium chloride to which a small amount of nitric acid has been added, and the latter by titration of known amounts of pure sodium chloride with potassium chromate as an indicator. A blank determination, using the same amount of indicator as in the sample, must be run and the correction subtracted from the sample titration. Ammonium thiocyanate and potassium thiocyanate are generally standardized by direct titration with standard silver nitrate solution, although the recrystallized salt may be used.

The evaluation of potassium ferrocyanide solutions is made with pure zinc oxide. This can be purchased in a high degree of purity and, after a preliminary drying for an hour at 105°C , is ready for use.

On account of its stability and the ease with which it is purified, potassium dichromate still remains an excellent standard substance for sodium thiosulphate solutions. Conflicting statements, however, have appeared in the literature concerning its use in the procedure. Vosburgh⁴³ states that if the solution is 0.2–0.4 *N* in HCl , contains 2–3 gm of potassium iodide for every five milliequivalents of dichromate, and is allowed to stand in the dark for 4–10 minutes, the reduction is quantitative. The solution is then diluted to 400 cc with distilled water, and titrated with the thiosulphate solution.

⁴³ W. C. Vosburgh, *J. Am. Chem. Soc.* 44, 2120 (1922).

On the other hand, Jander and Berte⁴⁴ add 15 cc of $N/10$ $K_2Cr_2O_7$ to 40 cc of 2 N KI and 40 cc of concentrated HCl . Complete liberation of iodine takes place in fifteen minutes. If the solution is titrated too quickly, too much thiosulphate is used. Their values, using this procedure, agreed exactly with those obtained by standardization of thiosulphate solution with potassium permanganate and pure iodine.

The reliability of the results, obtained by the use of this standard, has often been questioned. It has been suggested⁴⁵ that variations occur due to air oxidation of potassium iodide, and that the reaction is catalyzed by Cr^{+++} ions. Teis⁴⁶ found that variable results were obtained when the concentration of potassium iodide, and the time of standing were varied.

Potassium iodate and potassium bromate are satisfactory standards for thiosulphate solutions, but unsatisfactory from the standpoint of their low equivalent weights. Milstead,⁴⁷ however, reporting on the standardization of iodine and thiosulphate solutions, states that normalities obtained by use of iodine and unpuri-

⁴⁴ G. Jander and H. Berte, *Z. anorg. allgem. Chem.* **113**, 73 (1924).

⁴⁵ K. Bottger and W. Bottger, *Z. anal. Chem.* **69**, 146 (1926).

⁴⁶ R. V. Teis, *J. Gen. Chem. (U.S.S.R.)* **1**, 845 (1931); *Chemical Abstracts* **27**, 39 (1933).

⁴⁷ K. L. Milstead, *J. Assoc. Official Agri. Chem.* **22**, 567 (1939).

42 The Standardization of Volumetric Solutions

fied analytical grade potassium iodate do not agree, and that some impurity was present which liberated more iodine than a corresponding amount of iodate. The amount of this impurity, which was thought to be sodium iodate, appeared greater after recrystallization.

The use of potassium iodide in the standardization of solutions of low normality has been suggested by Hurka.⁴⁸ Briefly, the iodide is oxidized by bromine to iodate, which, in turn, is reacted with sulphuric acid, liberating iodine, which is titrated with the thiosulphate.

Potassium permanganate⁴⁹ has been used as a standard for sodium thiosulphate, and accurate results were obtained, providing that the conditions were strictly adhered to. The reaction between KMnO_4 and KI takes place in 50–125 cc of 0.7–0.1 N HCl or H_2SO_4 . After standing 2–5 minutes, the solution is diluted to 600 cc and titrated.

Potassium biiodate,⁵⁰ oxalic acid,⁵¹ and copper^{52, 53}

⁴⁸ W. Hurka, *Mikrochemie ver. Microchim. Acta* 28, 294 (1940).

⁴⁹ J. M. Hendel, *Z. anal. Chem.* 63, 321 (1923).

⁵⁰ M. Koenig, *Chimie et industrie*, Special No. 116–7 (Sept. 1925).

⁵¹ N. A. Tananaev and N. A. Lazarkevich, *J. Russ. Phys. Chem. Soc.* 61, 1909 (1929); *Chemical Abstracts* 24, 3456 (1930).

⁵² T. F. Buerer and C. M. Mason, *Ind. Eng. Chem., Anal. Ed.* 1, 68 (1929).

⁵³ S. Popoff, Margaret Jones, C. Rucker and W. W. Becker, *J. Am. Chem. Soc.* 51, 1299 (1929).

have been suggested as standard substances for thiosulphate solutions. Potassium biiodate can be obtained in a high state of purity, but possesses a low equivalent weight. The titration is carried out in a solution slightly acid with HCl.

If sodium thiosulphate is decomposed by HCl and converted to Na_2CO_3 by ignition with oxalic acid, the Na_2CO_3 may be titrated with standard acid, and the thiosulphate solution evaluated in this manner.

The use of copper * as an analytical standard must depend on the purity of the sample. Copper produced electrolytically is the best source. It is dissolved in sulphuric acid, evaporated to dryness, and taken up in distilled water. The reaction proceeds in a neutral, or nearly neutral, solution in the absence of salts. Potassium iodide is then added to reduce the copper. Acid concentration affects the determination by lessening the amount of iodine liberated, and should not be over 0.2 N in sulphuric acid.

Several standard substances are available for the evaluation of iodine solutions. A method commonly used is the titration of the unknown solution with previously standardized sodium thiosulphate. This is necessarily open to errors, which may be additive, arising from the standardization of the thiosulphate solution.

* See also, Copper Sulphate as a Standard for Thiosulphate Titrations, a review with discussion of the literature, N. Schoorl, *Pharm. Weekblad* 76, 1441 (1939).

44 *The Standardization of Volumetric Solutions*

Sodium thiosulphate pentahydrate is suitable as a standard substance. According to Kolthoff,⁵⁴ its range of stability is great. Below 23% relative humidity it weathers, and above 69% it deliquesces. The anhydrous salt is not recommended, as it is strongly hygroscopic.

Arsenious acid is a very satisfactory standard. It is stable and easily obtainable pure.

Sodium acetomercurithymol sulphonate⁵⁵ may be obtained in a high degree of purity. It has a high molecular weight, and reacts with iodine by displacement of the acetomercuric group. It is stated to give more accurate results than arsenious oxide.

Hydrazine reacts with iodine according to the following equation:



It is used in the form of hydrazine sulphate, and the reaction takes place in a solution alkaline with sodium bicarbonate. A disadvantage is its low equivalent weight.

Ammonium triiodate,⁵⁶ silver nitrate,⁵⁷ and potassium

⁵⁴ I. M. Kolthoff and N. H. Furman, *Volumetric Analysis, Vol. II* (1929), p. 360.

⁵⁵ C. V. Bordeianu, I. N. Petrescu, L. Staicovici, *Bull. Soc. Stiinte Farm. Romania* 4, 473 (1939); *Chimie et industrie* 43, 458.

⁵⁶ E. Riegler, *Bull. assoc. chim. suc. dist.* 24, 528; *Chemical Abstracts* 1, 705 (1907).

⁵⁷ V. E. Pavloc and S. D. Shein, *J. Russ. Phys. Chem. Soc.* 39, 943; *Chemical Abstracts* 2, 772 (1908).

stannous diaquotetrachloride ($\text{K}_2\text{SnCl}_4 \cdot 2 \text{H}_2\text{O}$)⁵⁸ have also been proposed as iodometric standards.

The usual method of standardization of potassium permanganate is by means of oxalic acid or sodium oxalate. Hill and Smith⁵⁹ recrystallized oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$), and found that values obtained with permanganate agreed within 0.025% with those obtained using Bureau of Standards sodium oxalate. The vapor pressure of the hydrate at ordinary temperatures is slightly less than that of air at the same temperature. There is, therefore, danger of water condensing as a film on the surface of the crystals. Treadwell and Johner⁶⁰ recommend drying the recrystallized and powdered acid in a stream of air which has been passed through a mixture of equal parts of hydrated and hydrous acid. The results, using this procedure, are comparable to those obtained by use of sodium oxalate. Calcium oxalate,⁶¹ prepared from pure calcium oxide, has been used as a standard substance, and satisfactory results are claimed for it.

The use of metallic silver⁶² has been proposed, and

⁵⁸ T. Karantarsis and L. Capatos, *Compt. rend.* 194, 1839 (1932).

⁵⁹ A. E. Hill and T. M. Smith, *J. Am. Chem. Soc.* 44, 546 (1922).

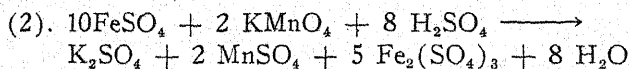
⁶⁰ W. D. Treadwell and H. Johner, *Helv. Chim. Acta* 7, 528 (1924).

⁶¹ E. Little and W. H. Beisler, *J. Am. Leather Chem. Assoc.* 14, 613 (1919).

⁶² N. A. Tananaev, *Z. anorg. allgem. Chem.* 136, 193 (1924).

46 *The Standardization of Volumetric Solutions*

the standardization of permanganate by it is obtained in the following manner: Ferric alum (0.5–1.0 gm) is dissolved in 100 cc of 7 *N* H₂SO₄ in an Erlenmeyer flask. The solution is saturated with CO₂, and 0.25–0.35 gm silver added. After the silver has dissolved, the solution is cooled rapidly, phosphoric acid added until the solution is colorless, and titrated with permanganate. The reactions involved take place as follows:



The use of iron, Mohr's salt, and arsenious oxide is not entirely satisfactory, since they all possess disadvantages. The purity of iron and Mohr's salt is questionable, and if it is necessary to establish the purity of these compounds by some other means, they lose their significance as standard substances. Ferric ammonium sulphate, which can be obtained pure by recrystallization, may be used as a standard, first reducing all the ferric iron to ferrous iron. Its keeping qualities are not good. The reaction with arsenious oxide does not proceed smoothly. Complex compounds are formed, and the end point is not well defined. Potassium ferrocyanide has been used as a standard substance, but the end point, which is difficult to detect, offsets the advantage of a high equivalent weight. Titration must take

place in dilute solution. DeBeer and Kjort⁶³ have used ferrocyanide for the standardization of dilute solutions, with erioglaucine as an indicator.

Evidence has been presented⁶⁴ to show that results of standardization of permanganate with sodium oxalate are not reliable to less than 1 part in 1000. Fused potassium iodide, titrated by Andrew's method to ICl, shows agreement within 0.03%, and may be regarded as a more reliable standard.

Further work⁶⁵ with potassium iodide for standardization of strong oxidizing agents such as permanganate and ceric sulphate involves the use of acetone. The iodide is dissolved in water acid with H_2SO_4 , and pure acetone added. The solution is titrated with the oxidizing agent, using three drops of 0.025 *N* ferrous phenanthroline sulphate as an indicator. The end point is reached when the solution remains colorless for thirty seconds. The results are generally low, due to a reaction between acetone and the oxidizing agent.

⁶³ E. J. deBeer and A. M. Hjort, *Ind. Eng. Chem., Anal. Ed.* 7, 120 (1935).

⁶⁴ I. M. Kolthoff, H. A. Laitinen and J. J. Lingane, *J. Am. Chem. Soc.* 59, 429 (1937).

⁶⁵ I. M. Kolthoff and H. A. Laitinen, *J. Am. Chem. Soc.* 61, 1690 (1939).

CHAPTER V

Standard Solutions of Acids and Bases

STANDARDIZATION OF HYDROCHLORIC ACID

Molecular Weight: 36.465	HCl
Equivalent Weight: 36.465	
Grams of Constant Boiling Acid/Liter for	
1 Normal Acid	180.193 gm
0.5 " "	90.097 gm
0.1 " "	18.019 gm

Preparation of Constant Boiling Acid

Since ordinary concentrated hydrochloric acid ¹ varies slightly in strength, it would seem useful to have some definite standard solution which would not vary in percentage composition. Hulett and Bonner ² recommended the use of constant-boiling acid for standard solutions. Foulk and Hollingsworth ³ made an extremely accurate investigation. They recommend start-

¹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

² G. A. Hulett and W. D. Bonner, *J. Am. Chem. Soc.* 31, 390 (1909).

³ C. W. Foulk and M. Hollingsworth, *J. Am. Chem. Soc.* 45, 1220 (1923).

ing with hydrochloric acid solution of specific gravity 1.18. After three-quarters of the mixture have been distilled, the receivers are changed and the distillation continued until only a few cubic centimeters are left in the still. This last distillate is considered to be constant-boiling acid. The speed of distillation has very little influence on the acid content. If, however, the original acid is diluted to a specific gravity of 1.0959 at 25° C, three-quarters of the distillate may be used. Discard the first quarter and continue distillation until only 50–60 cc are left. In this way, it is easy to obtain a definite standard solution within an accuracy of 0.05 per cent.⁴ Barometric pressure must be recorded, as the percentage composition varies. The following table (after Foulk and Hollingsworth)³ gives the composition of constant-boiling acid at various pressures.

Pressure during Distillation mm of Mercury	% HCl Referred to Vacuum	Wt. of Distillate Containing 1 Mol of HCl when Weighed on Air
780	20.173	180.621
770	20.197	180.407
760	20.221	180.193
750	20.245	179.979
740	20.269	179.766
730	20.293	179.551

Store the constant-boiling acid in glass-stoppered bottles. From the barometric pressure, calculate the percentage composition and label the bottles accordingly.

⁴ Kolthoff and Furman, *Volumetric Analysis Vol. II*, 74 (1929).

Standardization of Normal and Half Normal Acid with Sodium Carbonate

If the distillation of constant-boiling acid has been carried out at 760 mm, weigh out accurately 180.193 gm and 90.097 gm respectively for normal and half normal acid and make up to 1 liter with distilled water; otherwise weigh accurately equivalent amounts depending on the barometric pressure at the time of distillation.

According to Lunge, sodium bicarbonate is quantitatively converted into the carbonate by heating to 270–300° C. The procedure is as follows: Place 10 gm of the bicarbonate ⁵ in a silver crucible, and place in a shallow sand bath, imbedding the crucible so that the level of the sand is slightly above the level of bicarbonate in the crucible. Suspend a thermometer in the crucible in such a way that it acts as a stirring rod. Heat the sand bath so that the temperature rises at the rate of 5° C a minute, stirring the bicarbonate continually. This stirring is important, especially when relatively large amounts are to be converted to carbonate. After heating between 270 and 300° C for at least half an hour, the crucible is transferred to a desiccator and cooled. A recent paper by Smith and Croad ⁶

⁵ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **18**, 759 (1926).

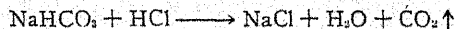
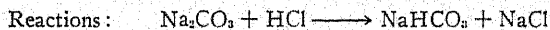
⁶ G. F. Smith and G. F. Croad, *J. Ind. Eng. Chem., Anal. Ed.* **9**, 141 (1937).

has shown that an appreciable error results when the temperature is allowed to exceed 300° C. The carbonate is transferred to a bottle having a tight-fitting, ground glass stopper. When weighing, the bottle should be opened only for brief intervals, and the weighing accomplished as quickly as possible, because of the fact that carbonate changes to the monohydrate rapidly.

If, for any reason, it is inconvenient to prepare carbonate from the bicarbonate, it is possible to use an analytical grade sodium carbonate, after washing with alcohol and drying at 100° C, since the chief impurity is sodium hydroxide, which is soluble in alcohol.

Procedure for Standardization

Weigh out sufficient sodium carbonate to give a titration of around 40 cc. In the case of normal acid, use 2.12 gm, and 1.06 gm for half normal acid. Dissolve the carbonate in the smallest possible quantity of water. Titrate, using methyl yellow as an indicator, to the first change. Just before the end point is reached, the solution should be stirred or shaken vigorously to remove carbon dioxide.



Calculations: Equivalent weight of $\text{Na}_2\text{CO}_3 = 53.0$

$$\text{Normality} = \frac{\text{Weight of Na}_2\text{CO}_3}{0.053 \times \text{Titration in cc}}$$

52 The Standardization of Volumetric Solutions

Standardization of Tenth Normal Acid by Precipitation as Silver Chloride

Tenth normal acid is prepared by accurately pipetting 100 cc of normal acid into a volumetric flask and diluting to one liter. It is standardized as follows: Pipette 50 cc portions into 250 cc beakers. Add an excess of silver nitrate solution to precipitate the acid as silver chloride. Bring to a boil to coagulate the precipitate. Let stand in the dark until cool, and filter through previously dried and weighed Gooch crucibles.



$$\text{Mol wt. AgCl} = 143.34 \quad 1 \text{ cc HCl} \approx 0.14334$$

$$\text{Calculations: Normality} = \frac{\text{Wt. of silver chloride}}{50 \times 0.14334}$$

Alternative Method of Standardization Using Borax

Borax ⁷ has long been recognized as a primary standard for acids. The greatest obstacle, however, has been the difficulty in preparing the anhydrous salt and preserving it in the anhydrous state. In an article,^{8, 10} it is stated that borax, recrystallized as the decahydrate from water and kept over a solution of sodium bromide having a relative humidity of 60%, is extremely stable over a long period. Added to this is the advantage that borax does not lose water of crystallization during the time of weighing.

⁷ Kolthoff and Furman, *Volumetric Analysis Vol. II*, 93 (1929).

Pure borax may be prepared as follows⁸: 45 gm of borax are added to 150 cc of water at room temperature, stirred well, and allowed to stand for several hours. The borax is filtered off through a Büchner funnel, washed twice with water, then with two portions of 95% ethyl alcohol, and finally twice with ethyl ether, each washing being followed by suction to remove the wash liquid. Use 5 cc of alcohol and ether for every 10 gm of borax. Transfer the crystals to a watch glass, and allow them to stand at room temperature a short time to permit evaporation of the ether, then transfer them to a desiccator containing a saturated sodium chloride solution as a desiccant. It was found that sodium chloride could be substituted for sodium bromide, since the relative humidity of the saturated solution⁹ is 60%. To insure the crystals reaching equilibrium, they should be left in the desiccator for a week before using.

Standardization of Normal, Half Normal, and Tenth Normal Acid

Prepare the normal solutions in accordance with the instructions given in the preceding methods.

Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, has a molecular weight of 381.43, and an equivalent weight of 190.76, which

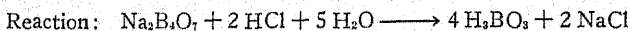
⁸ F. H. Hurley, *J. Ind. Eng. Chem., Anal. Ed.* 8, 220 (1936).

⁹ Kolthoff and Sandell, *Inorg. Quant. Analysis* (1929), 123.

54 *The Standardization of Volumetric Solutions*

means that large samples can be used for standardization, thus reducing the error in weighing.

The procedure is as follows: Weigh out 6.00 gm, 3.00 gm, and 0.65 gm respectively for normal, half normal, and tenth normal acid. Dissolve in the smallest quantity of distilled water. Add several drops of methyl red and titrate to the first visible change.



$$\text{Calculations: Normality} = \frac{\text{Wt. of Borax}}{0.19076 \times \text{Titration in cc}}$$

Note: In the standardization of tenth normal acid, it is necessary to boil the water first to remove carbon dioxide, since failure to do so introduces a real error in the standardization. In the case of normal and half normal acid, this precaution is not necessary.

Standardization of Normal, Half Normal, and Tenth Normal Acid with Thallous Carbonate

Thallous carbonate, with its high equivalent weight (468.79), is an excellent primary standard for acids and has also been used for the standardization of iodate solutions.

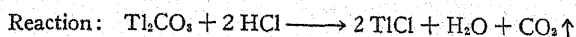
The following procedure for the standardization of acids is based on the method recommended by Berry.¹¹

A suitable quantity of the salt (or a corresponding volume of solution) is dissolved in distilled water and

¹⁰ F. H. Hurley, *J. Ind. Eng. Chem., Anal. Ed.* 9, 237 (1937).

¹¹ A. J. Berry, *Analyst*, 64, 27 (1939).

titrated, using methyl orange as an indicator.* The pH at the end point is 3.8.



$$\text{Calculations: Normality} = \frac{\text{Wt. Ti}_2\text{CO}_3}{0.46879 \times \text{cc Titration}}$$

STANDARDIZATION OF SULPHURIC ACID

Molecular Weight: 98.08

H_2SO_4

Equivalent Weight: 49.04

Preparation of the Solution

Weigh accurately the amount of acid ¹² necessary to give the required normality, taking into consideration the strength of the acid as recorded on the original container. Add cautiously to a relatively large amount of water, and when cool, transfer to a volumetric flask and make up to volume.

Standardisation with Barium Chloride

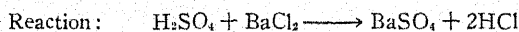
Pipette 25 cc of the volumetric solution into a 400 cc beaker, add 250 cc of distilled water and 3 cc of concentrated hydrochloric acid. Heat to boiling and precipitate at the boil with 10% barium chloride. Allow

*Hickman and Linstead [*J. Chem. Soc.* **121**, 2502 (1922)] recommend screening the methyl orange indicator with xylene cyanine FF.

¹² Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem., Anal. Ed.* **17**, 756 (1925).

56 The Standardization of Volumetric Solutions

the barium chloride¹² to run in drop by drop, stirring vigorously meanwhile. Popoff¹³ has shown that the temperature at which the barium sulphate is precipitated influences greatly the size of the crystals. Cover the beaker with a watch glass and let the precipitate stand over night on the steam plate. Filter, hot, through a quantitative filter paper, and wash the precipitate at least ten times with hot water, or until the filtrate gives no precipitate with silver nitrate. Ash carefully in a platinum crucible, or a clean porcelain crucible, to constant weight.



Calculations: Factor $\frac{\text{H}_2\text{SO}_4}{\text{BaSO}_4} = \frac{98.08}{233.42} = 0.4202$

$$0.4202 \times \frac{1000}{25} \times \text{wt. of ppt.} = \text{wt. of H}_2\text{SO}_4 \text{ in gm/l}$$

$$\text{Normality} = \frac{49.04}{\text{wt. of H}_2\text{SO}_4}$$

The standardization of sulphuric acid is accomplished most accurately by precipitation as barium sulphate. However, the methods involving the use of borax or carbonate, as described under hydrochloric acid, give equally accurate results.

Note: Picric acid (10 cc of a saturated solution) may be added to the sample of sulphuric acid to be standardized, before precipitation as barium sulphate. The solution is brought to boiling and the

¹³ S. Popoff and E. W. Neuman, *Ind. Eng. Chem., Anal. Ed.* 2, 45 (1930).

usual procedure for precipitation followed. If the solution is boiled gently for 5-10 minutes, and then allowed to stand on a steam plate for an hour, the precipitate may be filtered, ignited, and weighed. The results obtained may not be strictly accurate, since, if the filtrate from this procedure is allowed to stand over night, it is possible to obtain a slight amount of precipitate, representing barium sulphate, which, at the time of filtration, was in the colloidal state. It is also important that the acidity, after precipitation, should not be too high, since hydrochloric acid exerts a solvent effect, or possibly a peptizing action on freshly precipitated barium sulphate. Picric acid may contain soluble sulphate as an impurity. If there is any doubt as to the purity, it is necessary to run a blank determination on the amount of picric acid ordinarily used in the determination.

STANDARDIZATION OF SODIUM HYDROXIDE

Molecular Weight: 40.00
Equivalent Weight: 40.00

NaOH

Preparation of the Solution

Standard solutions of sodium hydroxide¹⁴ should be prepared from a concentrated stock solution.^{15, 16} This is a 50% solution, so called Sörenson's "oily alkali," and is made by dissolving one pound of pellet caustic in 450 cc of distilled water. The solution will be cloudy, due to carbonate¹⁷ which is always present. Let the solution stand for several days or until the carbonate has settled out and the liquid is clear, before using. If

¹⁴ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

¹⁵ Hillebrand and Lunden, *Applied Inorganic Analysis* (1929), 139.

¹⁶ Kolthoff and Furman, *Volumetric Analysis Vol. II* (1929), 77.

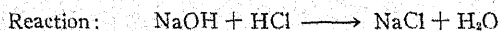
¹⁷ J. E. S. Han and T. Y. Chao, *J. Ind. Eng. Chem., Anal. Ed.* 4, 229 (1932).

58 *The Standardization of Volumetric Solutions*

it is necessary to use immediately, the solution may be centrifuged.¹⁸ The solution is best kept in a Pyrex Erlenmeyer, tightly closed with a rubber stopper.

Standardization with Hydrochloric Acid

Weigh out the equivalent of alkali by withdrawing the stock solution by means of a pipette, and transferring to a weighing bottle. If tenth normal alkali, or less, is to be prepared, make up to volume with water which has been previously boiled to expel carbon dioxide. Pipette 25 cc of previously standardized hydrochloric acid into an Erlenmeyer flask and titrate to an end point, using phenolphthalein as an indicator. The accuracy of this standardization will depend upon the accuracy with which the normality of the hydrochloric acid was determined.



Calculations: $N_{\text{NaOH}} \times V_{\text{NaOH}} = N_{\text{HCl}} \times V_{\text{HCl}}$

where N = normality and V = volume of solution used

Standardization with Potassium Acid Phthalate^{19, 20}

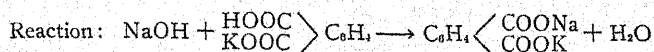
Potassium acid phthalate may be obtained pure from the Bureau of Standards, or the pure salt may be re-

¹⁸ N. Allen and G. W. Low, *J. Ind. Eng. Chem., Anal. Ed.* 5, 192 (1933).

¹⁹ F. E. Dodge, *J. Ind. Eng. Chem.*, 7, 29 (1915).

²⁰ W. S. Hendrixson, *J. Am. Chem. Soc.* 37, 2353 (1915); 42, 724 (1920).

crystallized from water and dried at 105° C. Weigh a sufficient quantity of the salt to give a titration of about 40 cc. Dissolve in a small quantity of distilled water and titrate with alkali to an end point with phenolphthalein.

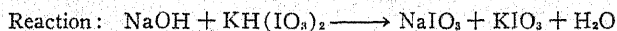


Calculations: The equivalent weight of potassium acid phthalate is 204.06

$$\text{Normality} = \frac{\text{Wt. of } \text{KHO}_2\text{C}_6\text{H}_4}{0.20406 \times \text{cc of alkali}}$$

Standardization with Potassium Bi-iodate

The salt may be obtained pure. If necessary, it can be recrystallized from water and dried at 105° C. It has the advantage of a high equivalent weight, and is not hygroscopic. Dissolve enough of the salt to give a titration of about 40 cc in a small quantity of distilled water and titrate using phenolphthalein as an indicator.



Calculations: The equivalent weight of potassium bi-iodate is 389.85

$$\text{Normality} = \frac{\text{Wt. of } \text{KH}(\text{IO}_3)_2}{0.3899 \times \text{cc of alkali}}$$

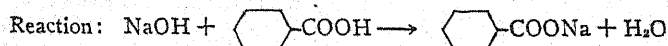
Standardization with Benzoic Acid

Pure benzoic acid may be purchased from the Bureau of Standards. It is, however, readily obtainable from other sources in a high degree of purity. Alcohol, which has been carefully neutralized to the phenolphthalein end point with alkali, is used as a solvent.



60 *The Standardization of Volumetric Solutions*

A weighed quantity of benzoic acid, sufficient to give a titration of around 40 cc, is dissolved in 25 cc of the neutralized alcohol and titrated to an end point



Calculations: The equivalent weight of benzoic acid is 122.46

$$\text{Normality} = \frac{\text{Wt. of benzoic acid}}{0.1225 \times \text{cc of alkali}}$$

Standard solutions of alkali should be stored in bottles made of alkali-resistant glass. Ordinary glass bottles are appreciably attacked on standing. As a precaution against contamination of the standard alkali from carbon dioxide in the air, it is well to equip the containers with a soda-lime tube.

STANDARDIZATION OF POTASSIUM HYDROXIDE

Molecular Weight: 56.10

KOH

Equivalent Weight: 56.10

Preparation of the Solution

Potassium hydroxide,²¹ unfortunately, cannot be prepared carbonate-free as easily as sodium hydroxide, since potassium carbonate is appreciably soluble in the concentrated alkali. Kolthoff^{22, 23} suggests the follow-

²¹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

²² I. M. Kolthoff, *Z. Anal. Chem.* 61, 48 (1922).

²³ Kolthoff and Furman, *Volumetric Analysis Vol. II* (1929), 77.

ing method: Prepare a 1.1 *N* solution of potassium hydroxide. Add 50–80 cc of milk of lime and shake for one hour. Allow to settle for several days and siphon off the clear liquid. The solution must be protected from the carbon dioxide of the air by means of a soda lime tube. After determining the normality of this stock solution, it may be diluted to the desired strength. If the directions are properly carried out, the solution will contain no more than 1–2 mg of calcium per liter. The presence of carbonate may be determined qualitatively by adding some of the alkali to a test tube containing *N*/2 barium nitrate or chloride, closing the tube quickly after addition, and shaking. No turbidity should form after ten minutes standing.

Carbonate-free potassium hydroxide may also be prepared by dissolving the alkali in a small quantity of alcohol. After the carbonate settles out, the clear solution is decanted into a volumetric flask containing previously boiled distilled water, and made up to volume.

Standardization of potassium hydroxide is carried out in the same way as for sodium hydroxide (q.v.).

STANDARDIZATION OF BARIUM HYDROXIDE AND AMMONIA

Molecular Weight: 171.38
Equivalent Weight: 85.69

$\text{Ba}(\text{OH})_2$

Molecular Weight: 35.05
Equivalent Weight: 35.05

NH_4OH

62 *The Standardization of Volumetric Solutions*

Standard solutions of these alkalis are comparatively little used, and are, moreover, extremely hard to keep. The titer will vary from day to day, necessitating re-standardization each time the solution is used.

Preparation and Standardization of Barium Hydroxide

Barium hydroxide, which has been treated with barium chloride to reduce the solubility of barium carbonate, is best used for the standard solution. It must be kept carefully protected from the carbon dioxide of the air, and must be made up with previously boiled distilled water. It is most easily standardized against standard acid, using phenolphthalein as an indicator. (See directions for standardizing sodium hydroxide with hydrochloric acid.)

Preparation and Standardization of Ammonia

Ammonia,²⁴ due to its volatility at ordinary temperatures, is very unsatisfactory as a standard reagent. Weigh, in a closed vessel, the approximate amount of ammonia and transfer quickly to a volumetric flask containing boiled distilled water. Stopper and mix, make up to volume, transfer to tightly stoppered container, and keep in a cool place. Standardize against hydrochloric acid, using methyl orange as an indicator. Methyl red may be preferred, since the transition range is sharper.

²⁴ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

SUPPLEMENTARY REFERENCES

The Stability of Constant Boiling Hydrochloric Acid, J. A. Shaw, *Ind. Eng. Chem.* 18, 1065 (1926).

The Composition of Hydrochloric Acid of Constant Boiling Point, W. D. Bonner and B. F. Branting, *J. Am. Chem. Soc.* 48, 3093 (1926).

The Composition of Constant Boiling Hydrochloric Acid at Pressures of 50–1220 millimeters, W. D. Bonner and A. C. Titus, *J. Am. Chem. Soc.* 52, 633 (1930).

The Boiling Points of Constant Boiling Hydrochloric Acids, W. D. Bonner and R. E. Wallace, *J. Am. Chem. Soc.* 52, 1747 (1930).

Anhydrous Sodium Carbonate for Standardization, L. Waldbauer, D. C. McCann, and L. F. Tuleen, *Ind. Eng. Chem., Anal. Ed.* 6, 336 (1934).

Thallous Carbonate as a Titrimetric Standard, R. Hac and K. Kamen, *Collection Czechoslov. Chem. Communications* 4, 145; cf. *Chem. Listy* 26, 6 (1932).

Thallous Carbonate as an Acidimetric Standard, Einar Jensen and Bailli Nilssen, *Ind. Eng. Chem., Anal. Ed.* 11, 508 (1939).

Determination of Sulphur in Rubber Compounds. I. Precipitation of Barium Sulphate in the Presence of Picric Acid, C. H. Lindsly, *Ind. Eng. Chem., Anal. Ed.* 8, 176 (1936).

Concerning Certain Organic Acids and Acid Anhydrides as Standards on Alkalimetry and Acidimetry, I. K. Phelps and L. H. Weed, *Am. J. Sci.* 26, 141 (1908); *Chemical Abstracts* 2, 2659 (1908).

Benzoic Acid as an Acidimetric Standard, G. W. Morey, *J. Am. Chem. Soc.* 34, 1027 (1912).

Use of Benzoic Acid as an Acidimetric Standard, S. V. Lipin, Z. E. Lukins, S. A. Konovalova, *Trav. inst. metrol. standardisation, U.R.S.S.* No. 5, 59 (in French 68) (1934).

Differential Potentiometric Titration IV: (a) Adaption of the Method of Hydrogen Electrodes, (b) Test of Standards for Precise Acidimetry, D. A. MacInnes and I. A. Cowperthwaite, *J. Am. Chem. Soc.* 53, 555 (1931).

CHAPTER VI

Standard Solutions of Precipitation Reagents

STANDARDIZATION OF POTASSIUM OR AMMONIUM THIOCYANATE

Molecular Weight: 97.17	KSCN
Equivalent Weight: 97.17	
Molecular Weight: 76.11	NH ₄ SCN
Equivalent Weight: 76.11	

Preparation of Potassium or Ammonium Thiocyanate

The thiocyanates are hygroscopic, and therefore, the theoretical amounts of the salts cannot be weighed with any accuracy. It is necessary to weigh out slightly more than the theoretical. Approximate amounts are weighed out, and made up to one liter. Of the two, ammonium thiocyanate¹ is better adapted for standard solutions.

Recent work by Kolthoff and Lingane² has shown that potassium thiocyanate,¹ when recrystallized and properly dried, is suitable for a primary standard.

¹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

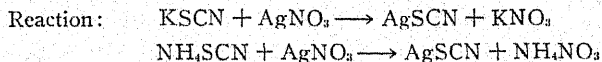
² I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.* 57, 2126 (1935).

Below a relative humidity of 45%, the dried material keeps well, but should be protected from light.

To prepare potassium thiocyanate for a standard solution, the reagent-grade salt may be dried at 150° C for three hours. If excessive moisture causes caking during the first hour of drying, the sample should be removed, the cake broken up by grinding and returned to oven for the remainder of the drying period.

Procedure

Pipette 25 cc of a standard solution of silver nitrate ³ into a 400 cc beaker, and add about 100 cc of distilled water. Now add 5 cc of a saturated solution of ferric ammonium alum ³ acidified with nitric acid, and titrate with the volumetric solution of thiocyanate to the first permanent appearance of a red brown coloration. Samples of silver nitrate of known purity may be titrated in the same manner.



Calculations: Standardization with standard silver nitrate

$$N_{\text{SCN}} = \frac{N_{\text{AgNO}_3} \times V_{\text{AgNO}_3}}{V_{\text{SCN}}}$$

Standardization with solid silver nitrate.
 Equiv. Wt. 169.89

$$\text{Normality} = \frac{\text{Wt. of AgNO}_3}{0.16989 \times \text{Titration in cc}}$$

³ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 18, 759 (1926).

66 *The Standardization of Volumetric Solutions*

Note: If ferric ammonium alum produces a cloudy solution in water, the addition of a few drops of nitric acid clears the solution. Ferric nitrate may be used in place of ferric alum.

The red brown color observed at the end point of the titration is due to the formation of ferric thiocyanate.

STANDARDIZATION OF SILVER NITRATE

Molecular Weight: 169.89

AgNO_3

Equivalent Weight: 169.89

Preparation of the Solution

Reagent-grade silver nitrate ⁴ may be used. This approaches 100% so closely that only a little more than the theoretical amount need be weighed out. The solution should be made up and transferred to a brown bottle as soon as possible. It is essential that the solution be kept free from dust and organic matter, in order to avoid any reduction. With this care, the solution should keep indefinitely.

Standardization with Sodium Chloride

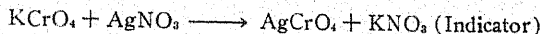
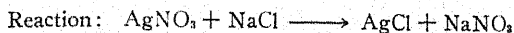
Weigh ⁵ 0.20–0.25 gm of precipitated sodium chloride and dissolve in 20 cc of distilled water in a casserole or evaporating dish. Add 1.5 cc of a 5% solution of potassium chromate ⁶ and titrate to the first permanent tinge of red. Titrate slowly with constant stirring.

⁴ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

⁵ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 20, 979 (1928).

⁶ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem., Anal. Ed.* 1, 171 (1929).

Standard Solutions of Precipitation Reagents 67



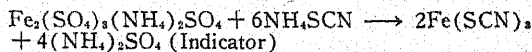
Calculations: The equivalent weight of sodium chloride is 58.45

$$\text{Normality} = \frac{\text{Wt. of NaCl}}{0.05845 \times \text{cc AgNO}_3}$$

Standardisation with Ammonium Thiocyanate

Silver nitrate may be standardized against a previously standardized solution of ammonium thiocyanate.

Pipette 25 cc of silver nitrate into a 400 cc beaker containing 200 cc of distilled water and 5 cc of saturated ferric ammonium alum. The solution is titrated with thiocyanate to the first appearance of a permanent red brown color.



Calculations: $N_{\text{AgNO}_3} \times V_{\text{AgNO}_3} = N_{\text{NH}_4\text{SCN}} \times V_{\text{NH}_4\text{SCN}}$

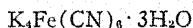
Kolthoff and Lingane⁷ state that potassium thiocyanate, recrystallized from water and dried for a short time at 200° C, can be used for standardizing silver nitrate solution.

Note: Pure sodium chloride may be prepared by passing hydrochloric acid gas, made by allowing concentrated sulphuric acid to drop slowly on solid sodium chloride, into a concentrated salt solution. The pure salt will precipitate. It is filtered on a Büchner funnel and washed with several small portions of distilled water. Dry at 105° C and store in a glass-stoppered bottle. Always dry the sodium chloride for an hour at 105° C before using to standardize silver nitrate solutions.

⁷ I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.* 57, 2126 (1935).

STANDARDIZATION OF POTASSIUM FERROCYANIDE

Molecular Weight: 422.33
Equivalent Weight: 211.17

*Preparation of the Solution*

Weigh out the required amount of the salt and make up to volume. The solution, on standing, oxidizes slightly, forming some ferricyanide. As diphenylamine⁸ and diphenyl benzidine are sometimes used as internal indicators in preference to the outside indicator uranyl nitrate, and are aided by the presence of ferricyanide, the solution is allowed to age for several weeks before standardizing, or a maximum of 150 milligrams of potassium ferricyanide per liter is added, whereupon the solution may be standardized immediately. If either diphenylamine or diphenyl benzidine is used, a 1% solution in concentrated H_2SO_4 is made up, and 0.2 cc used per 100 cc of solution. In using diphenylamine, a titration correction must be applied. Diphenyl benzidine, however, is independent of this correction. The color change is to a deep blue color in both cases. Temperature also affects the sensitivity of these indicators. If uranyl nitrate is used, a 1% solution in water is recommended.

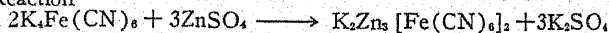
Standardization

Weigh out appropriate samples of pure zinc oxide

⁸ W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* 49, 356 (1927).

calculated to give titrations of around 40 cc. Dissolve in dilute H_2SO_4 and dilute to 100 cc. Add $(\text{NH}_4)_2\text{SO}_4$, heat to 60°C and titrate immediately. Do not let the temperature drop below 50°C . If it does, reheat the solution and continue the titration. If an internal indicator is used, the color change is from a light bluish green to a deep blue. In dilute solutions, this change is not evident. In the case of uranyl nitrate, the indicator is spotted on a white porcelain plate. When the end point is approached, the solution should be spotted for every 0.10 cc of ferrocyanide added. A dark brown ring or coloration developing within 2–3 seconds is taken as the end point.

Reaction



The titration is carried out in hot solution because at room temperature, although the above reaction goes to completion, the freshly formed zinc complex reacts with the uranyl nitrate indicator. It is gradually converted to an allotropic form which does not react with the indicator. Heating the solution converts it immediately to this latter phase.

Calculations

Since ferrocyanide is used, for the most part, in the determination of zinc, it is usually evaluated in terms of zinc oxide. In other words, $\frac{\text{Wt. of ZnO}}{\text{Titration in cc}}$ will represent the titer of the solution. A customary figure of 21.6 gm of potassium ferrocyanide gives approximately 1 cc \approx 0.006 gm zinc oxide.

70 *The Standardization of Volumetric Solutions*

SUPPLEMENTARY REFERENCES

Standardization of Silver Nitrate Solutions Used in Chemical Studies of Sea Water, T. G. Thompson, *J. Am. Chem. Soc.* **50**, 681 (1928).

Bartholow Park, *J. Am. Chem. Soc.* **54**, 180 (1932).

CHAPTER VII

Standard Solutions of Oxidizing Reagents

STANDARDIZATION OF IODINE

Atomic Weight: 126.92
Equivalent Weight: 126.92

I_2

Preparation of the Solution

Since there is always a possibility of iodine¹ containing chlorine, bromine, or water as impurities, it is usually advisable to resublime it. This may be done very simply, using the apparatus shown in Figure 1. The iodine crystals are heated slowly with a very small flame, and the iodine sublimes in crystals on the cooled portion of the water-cooled, round-bottom flask. The sublimed iodine is transferred to a glass-stoppered bottle.

In making standard solutions of iodine, it is necessary to dissolve the iodine in a solution of potassium

¹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

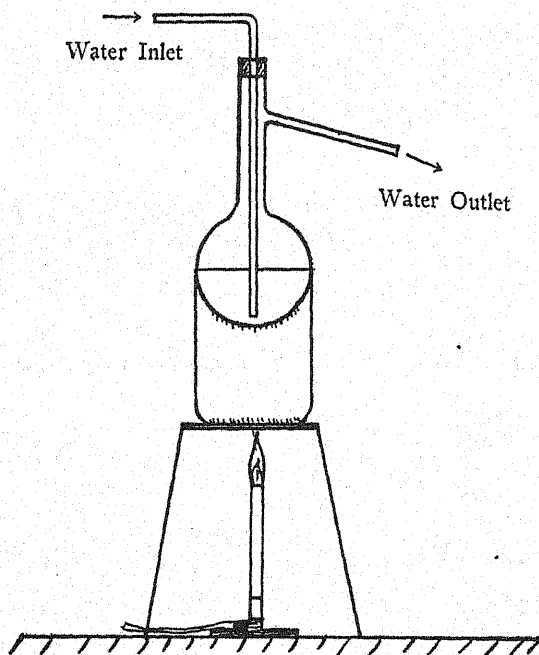


FIG. I

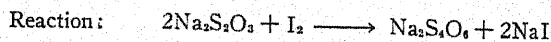
iodide.² Therefore, the following procedure is used in making a 0.1 *N* solution. Weigh accurately 12.692 gm of sublimed iodine into a glass-stoppered tall-form weighing tube. Dissolve 25 gm of potassium iodide in 35–40 cc of water. Uncover the weighing bottle and add about 20 cc of this solution. Swirl gently to dissolve the bulk of the iodine and transfer to a liter

² Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 19, 645 (1927).

volumetric flask. Rinse the weighing tube with the remainder of the iodide solution, quantitatively transferring all of the iodine to the liter flask. Add no water until all the iodine has dissolved. After diluting to volume, transfer to a brown bottle. Iodine solutions are not stable to light, decomposition taking place with the formation of hydriodic acid. A high room temperature also affects them to the point of volatilizing some iodine. Hence, it is necessary to standardize the solutions frequently.

Standardization against 0.1 N Thiosulphate

Aliquots of previously standardized thiosulphate solution are transferred to Erlenmeyer flasks and diluted to 150 cc. The solution is titrated with the iodine to be standardized to a permanent blue end point, using freshly prepared starch as an indicator.



Calculations: $N_{\text{I}_2} \times V_{\text{I}_2} = N_{\text{Na}_2\text{S}_2\text{O}_3} \times V_{\text{Na}_2\text{S}_2\text{O}_3}$

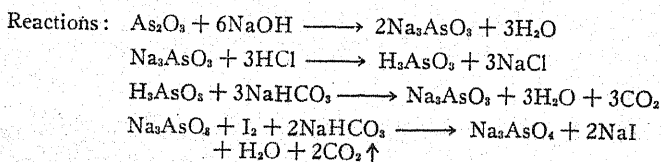
Standardization with Arsenious Oxide

Weigh accurately 0.2000 gm of arsenious oxide,^a which will give a titration of 40 cc, and dissolve in 10 cc of *N* sodium hydroxide. Dilute to 150 cc and add HCl until the solution is faintly acid. Add, cautiously, enough of a concentrated solution of sodium bicarbonate to represent 2–3 gm of the salt. Add starch and titrate to a permanent blue end point. Cover the

^a Obtainable from the U. S. Bureau of Standards.

74 The Standardization of Volumetric Solutions

beakers with a watch glass while adding the bicarbonate:



The arsenious oxide dissolves more readily in sodium hydroxide than in bicarbonate. The titration, however, must be carried out in a solution alkaline with bicarbonate. It is for this reason that the solution containing an excess of caustic is neutralized with acid.

Calculations: The equivalent weight of arsenious oxide is 49.46

$$\text{Normality} = \frac{\text{Wt. of As}_2\text{O}_3}{0.04946 \times \text{cc Titration}}$$

Recrystallized sodium thiosulphate may be used as a primary standard. It should be kept in a container at a definite humidity, such that only the pentahydrate can exist. A stock solution of arsenious oxide may be prepared by accurately weighing 4.946 gm, dissolving in 40 cc of 1 *N* NaOH, acidifying with HCl until neutral to litmus, and making up to one liter. Kolthoff ⁴ states that a solution made according to these directions is stable over a long period.

Note: The importance of potassium iodide should not be underestimated. It is essential that potassium iodide be present, particu-

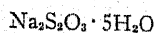
⁴ Kolthoff and Furman, *Volumetric Analysis*, Vol. I (1929), 235.

larly in cases where the iodine titration is small; one cc of 10% solution is sufficient for a volume of 200–300 cc. Omission causes consumption of iodine. Potassium iodide is, of course, supplied by the standard solution, but if the probable titration is unknown, it is safer to add more.

The reason for adding the iodide to the standard solution is that it increases the solubility, and decreases the vapor pressure of the iodine, thus reducing the possibility of loss by volatilization.

STANDARDIZATION OF SODIUM THIOSULPHATE

Molecular Weight: 248.19



Equivalent Weight: 248.19

Preparation of the Solution

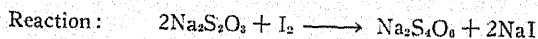
For a 0.1 *N* solution, 24.82 gm are weighed out, dissolved, and made up to one liter. The anhydrous salt should never be used for volumetric solutions because of the uncertainty in its composition. The hydrated salt ⁵ is obtainable in a high degree of purity in the market and may be used without further purification. It has been stated that a 0.1 *N* solution can be made by simply weighing accurately the required amount of the salt and diluting to exact volume, but this is not safe practice, since discarding the effect of manual errors and errors due to uncalibrated apparatus, thiosulphate in commercial lots sometimes shows evidence of the presence of the lower hydrates, which are noticeable as a powdery deposit on the surface of the crystals.

⁵ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 18, 759 (1926).

76 The Standardization of Volumetric Solutions

Standardization with Iodine

A previously standardized solution of iodine may be used. An aliquot is titrated with the thiosulphate. Add starch near the end point and titrate to the disappearance of the blue color. Iodine itself may be used as a primary standard. Sublime the iodine according to the directions given under the *Standardization of Iodine*. Weigh accurately a small weighing tube with a ground glass stopper containing 2-3 gm of potassium iodide in 2-3 cc of water. The heat of solution of potassium iodide is negative, and it is necessary to wait until the weighing tube and solution have attained room temperature before weighing. Now add quickly about 0.5 gm of sublimed iodine and weigh again. The difference is the exact amount of iodine added. The stoppered weighing tube is transferred to a 300 cc Erlenmeyer flask containing 150 cc of distilled water and allowed to open *only under the water*. The solution is now titrated in the usual manner.



$$\text{Calculations: } N_{\text{I}} \times V_{\text{I}} = N_{\text{Na}_2\text{S}_2\text{O}_3} \times V_{\text{Na}_2\text{S}_2\text{O}_3}$$

Iodine has an equivalent weight of 126.92

$$\text{Calculations: Normality} = \frac{\text{Wt. of Iodine}}{0.12692 \times \text{cc Titration}}$$

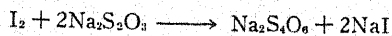
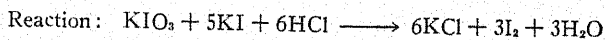
Standardization with Potassium Iodate

Potassium iodate may be purchased in a high state of purity, or the commercial salt may be recrystallized

from water and dried at 180° C. Its great disadvantage is its low equivalent weight: 35.67.

Weigh out 0.15 gm of the salt and dissolve in 50 cc of distilled water. Add 20 cc of a 15% potassium iodide solution. Make the volume up to 150 cc and add 5 cc of concentrated HCl. Titrate immediately. Add starch near the end point and titrate to the disappearance of the blue color.

Note: In all titrations where iodine is liberated, it is best to carry out operations in an Erlenmeyer flask, or stoppered flask, to minimize loss of iodine.



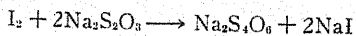
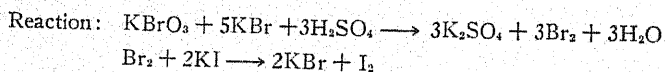
$$\text{Calculations: Normality} = \frac{\text{Wt. of KIO}_3}{0.03567 \times \text{cc Titration}}$$

Standardization with Potassium Bromate

The same disadvantage exists with this salt as with the iodate, namely, its low equivalent weight, which is 27.84. It also has the disadvantage of sometimes containing bromide. This may be tested for, qualitatively, by adding 1–2 cc of 4 *N* H₂SO₄ to a 1% solution. After five minutes, no color should develop. The bromate-iodide-acid reaction does not take place as quickly as the iodate-iodide-acid. After addition of acid, it is necessary to let the mixture stand for several minutes before proceeding with the titration. Also, the concentration of the acid is an important factor. The following procedure is satisfactory: Weigh 0.12 gm of potas-

78 The Standardization of Volumetric Solutions

sium bromate into an Erlenmeyer flask, and dissolve in 50 cc of distilled water. Add 20 cc of 15% potassium iodide solution and dilute to 150 cc. Now add 15 cc of 10% H_2SO_4 , stopper the flask, and let stand for three minutes. Titrate, using starch as an indicator.



Calculations: The equivalent weight of KBrO_3 is 27.84

$$\text{Normality} = \frac{\text{Wt. of } \text{KBrO}_3}{0.02784 \times \text{Titration in cc}}$$

Standardization with Potassium Dichromate^{6, 7, 8}

Potassium dichromate⁶ is another salt which can be obtained in a high degree of purity. Impure dichromate may readily be recrystallized from water and dried at 200° C. Under the right conditions of acidity, potassium dichromate is very satisfactory as a standard substance. The reaction first passes through an induction period and then proceeds at increasing speed. The acidity of the solution, to a great extent, controls the reaction. If, for instance, the acidity is in the neighborhood of 0.5–1.0 normal, it is necessary to let the solution

⁶ W. C. Vosburgh, *J. Am. Chem. Soc.* 44, 2120 (1922).

⁷ H. H. Willard and Philena Young, *J. Ind. Eng. Chem., Anal. Ed.* 7, 57 (1935).

⁸ W. C. Bray and H. E. Miller, *J. Am. Chem. Soc.* 46, 2204 (1924).

⁹ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

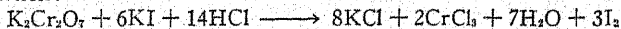
stand for 5 minutes before titrating; but, if the acidity is 1.4 to 1.5 normal, the solution may be titrated immediately. However, the acidity must not be too high, otherwise, the possibility of air oxidation enters, which may lead to erroneous results. It is, therefore, extremely important to adjust the acidity to the right concentration, if correct results are to be obtained.

The practice of weighing out potassium dichromate, diluting to a specific volume, and assuming this to be exactly 0.1 normal, although sufficiently accurate for routine procedure, should not be acceptable for accurate work.

Weigh 0.12–0.15 gm of previously dried dichromate and dissolve in 50 cc of distilled water. Add 15 cc of 15% KI, and 7 cc of concentrated HCl. Titrate immediately and add starch as an indicator. The end point should be observed carefully so as not to overtitrate. The color change is from blue to the green color of chromic salts.

An alternate procedure may be used. Weigh out the sample and dissolve in 75 cc H₂O. Add 15 cc of 15% KI and 10 cc of concentrated HCl. Let stand for 5 minutes in the dark, dilute to 400 cc, and titrate.

Reaction:



Calculations: The equivalent weight of K₂Cr₂O₇ is 49.04

$$\text{Normality} = \frac{\text{Wt. of K}_2\text{Cr}_2\text{O}_7}{0.04904 \times \text{Titration in cc}}$$

Standardization with Copper or a Copper Salt

Copper of known purity, or a pure copper salt may be used as a standard substance. If copper is used, it should first be washed with alcohol and ether, to remove any oily material, polished bright with a suitable cleaner, rinsed with water, and again with alcohol, and finally dried for a short time at 105° C. Dissolve a suitable amount of the copper in 10 cc of 6 *N* H₂SO₄. Dilute to 35 cc with distilled water, add 15 cc of 15% KI, and titrate, using starch as an indicator. If the copper salt is used, dissolve the sample in 35 cc of distilled water, containing 5 cc of 6 *N* H₂SO₄. Add 15 cc of 15% KI, and titrate.

In a recent article, Huerre¹⁰ states that a large excess of potassium iodide must be present. Loss of CuI is due to the solubility in thiosulphate solution.

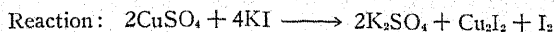
G. Bruhns¹¹ found that potassium thiocyanate was useful in this titration, reducing the amount of potassium iodide necessary and speeding up the reaction. Kolthoff¹² gives the following procedure using thiocyanate: 0.5 to 1 cc of *N* KI is added to the acidified copper solution, and then 10 cc of 10% potassium thiocyanate. Cupric thiocyanate is precipitated. The solution is titrated immediately. The dark brown thio-

¹⁰ R. Huerre, *J. Pharm. Chim.* **23**, 594 (1936).

¹¹ G. Bruhns, *Chem. Ztg.* **42**, 301 (1918).

¹² Kolthoff and Furman, *Volumetric Analysis*, Vol. II (1929), p. 430.

cyanate disappears, while the solution assumes the dark brown color due to iodine. Toward the end, starch is added and the titration continued to a permanent change of iodine-starch blue to leather yellow or dirty violet.



Calculations: The equivalent weight of copper is 63.57, and that of CuSO_4 is 160.63.

$$\text{Normality} = \frac{\text{Wt. of Cu, or CuSO}_4}{\text{Milliequivalent} \times \text{cc Titration}}$$

Note: Much has been written concerning the stability^{13, 14, 15} of thiosulphate solutions. Borax or sodium carbonate may be used as stabilizing agents, 0.1 gm Na_2CO_3 per liter, or 3.8 gm borax per liter. It has been the writer's experience that thiosulphate made up to volume with previously boiled distilled water and kept in clear glass bottles, in the dark, shows no appreciable diminution in titer after 1-2 months. On the other hand, solutions kept in brown glass bottles gave evidence of deterioration within two weeks. When stabilized with either borax or carbonate, however, they retained their titer for longer periods.

STANDARDIZATION OF POTASSIUM PERMANGANATE

Molecular Weight: 158.03

KMnO_4

Equivalent Weight: 31.61

Preparation of the Solution

Analytical-grade potassium permanganate¹⁶ may be used, or, to insure greater purity, since even the ana-

¹³ F. O. Rice, M. Kilpatrick, and W. Lemkin, *J. Am. Chem. Soc.* **45**, 1361 (1923).

¹⁴ Kolthoff and Furman, *Volumetric Analysis*, Vol. I (1929), p. 231.

¹⁵ Ph. Korkheimer, *Pharm. Ztg.* **80**, 1330 (1935).

¹⁶ Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **18**, 759 (1926).

lytical grade contains impurities, the salt may be recrystallized. Weigh out the required amount and dissolve in distilled water. Let the solution stand on the steam bath for 2–3 hours, or bring to a boil and heat 1 hour on the steam bath. This is necessary, since distilled water usually contains reducing substances. The solution is cooled and filtered either through a Gooch crucible or through a glass filtering funnel of the Büchner type having a porous plate. The manganese dioxide must be removed, since it acts as a catalytic agent, promoting the reduction of the permanganate. Make the filtered solution up to one liter, and transfer to a clean, clear glass bottle. Keep protected from the light. Some reduction will take place and, at intervals, it is necessary to filter off the manganese dioxide. Unless used constantly, it is best to restandardize before making a titration.

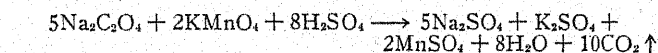
Standardization with Sodium Oxalate or Oxalic Acid

Sodium oxalate or oxalic acid purchased from the U. S. Bureau of Standards is recommended. Weigh out a 0.2–0.3 gm sample and dissolve in 50–60 cc of distilled water. Add 10 cc of 3 *N* H_2SO_4 , heat to 80° C or a little above, and titrate slowly with permanganate. Do not let the temperature fall below 80° C. The reaction starts very slowly at first, and it is best to add only a few drops of permanganate. When some oxidation has taken place resulting in the formation of manganous salt, the reaction goes rapidly, due to the

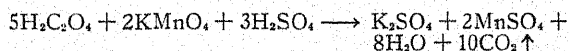
catalytic action of the manganous ions. The solution must be stirred rapidly throughout the determination. The end point is taken as the first permanent pink coloration. In their standardization of permanganate with sodium oxalate, Fowler and Bright¹⁷ correct for this error of overtitration, which they state to be 0.03–0.05 cc.

The presence of hydrochloric acid tends to give high results, due to oxidation of chloride ions to hypochlorous acid.

The reaction of permanganate, which is attended by side reactions, in its simplest form is as follows:



or



Calculations: The equivalent weight of sodium oxalate is 66.995, and that of oxalic acid, with two molecules of water, 63.03

$$\text{Normality} = \frac{\text{Wt. of sample}}{0.067 \text{ (or } 0.06303) \times \text{cc Titration}}$$

Ammonium oxalate,¹⁹ also, has been suggested as a primary standard.

¹⁷ R. M. Fowler & H. A. Bright, *J. Research Nat. Bur. Standards* 15, 493 (1935).

¹⁸ Treadwell and Hall, *Analytical Chemistry, Vol. II* (1930), 513.

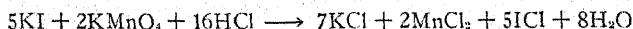
¹⁹ M. M. Kirilov, *J. Applied Chem.* 9, 2067 (in French) (1936).



84 *The Standardization of Volumetric Solutions*

Standardization with Potassium Iodide

The principle of this method depends upon the following equation:



Andrews²⁰ found that potassium iodide could be oxidized quantitatively by various reagents to colorless I_2 , and also, that unless the acid concentration was fairly high, hydrolysis of the I_2 took place. Kolthoff, Laitinen and Lingane,²¹ who have applied this method to the standardization of permanganate, give the following procedure:

To a glass-stoppered flask containing 25 cc of distilled water and 1 cc of concentrated HCl , add pure potassium bicarbonate to slight excess. A weighed sample of fused potassium iodide is next added, and then sufficient concentrated HCl , assuming a final volume of 350 cc, so that the solution is 3.7–5.5 N with respect to the acid. Cool in an ice bath and add 6 cc CCl_4 . Titrate with permanganate to the disappearance of the iodine color in the CCl_4 layer.

$$\text{Calculations: Normality} = \frac{\text{Wt. of KI}}{0.08299 \times \text{cc Titration}}$$

Note: Instead of the fused salt, potassium iodide, which has been dried at 200–220° C, may be used. The results may be slightly higher (0.02–0.03%) due to the retention of occluded water.

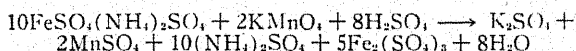
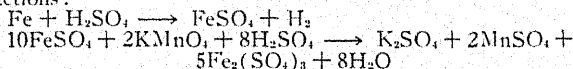
²⁰ L. W. Andrews, *J. Am. Chem. Soc.* 25, 756 (1903); *Z. anorg. allgem. Chem.* 36, 76 (1903).

²¹ I. M. Kolthoff, H. A. Laitinen and J. J. Lingane, *J. Am. Chem. Soc.* 59, 429 (1937).

Standardization with Iron Wire,¹⁸ Ferrous Sulphate, or Mohr's Salt

A suitable quantity of pure iron wire, or either of the two salts is weighed out and dissolved in dilute sulphuric acid. The solution is diluted to approximately 100 cc and run through a Jones reductor, to insure complete reduction of the ion. Add 5 cc of phosphoric acid (85%) and titrate with permanganate to the first permanent pink color. The advantage of adding phosphoric acid is that colorless complex phosphate ions are formed, and the end point is, therefore, sharper, since otherwise it is a reddish orange.

Reactions:



Calculations:

The equivalent weights used are:

$$\text{Fe} = 55.84$$

$$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 278.01$$

$$\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} = 391.90$$

$$\text{Normality} = \frac{\text{Wt. of sample}}{\text{Milliequivalent} \times \text{cc Titration}}$$

Pure iron (electrolytic) is available for standardization. Mohr's salt, which has the advantage of a high equivalent weight, is seldom obtainable pure. However, the salt may still be used as a standard, if first its reducing power is determined.

STANDARDIZATION OF POTASSIUM DICHROMATE

Molecular Weight: 294.21
 Equivalent Weight: 49.04

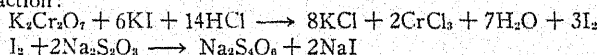
*Preparation of the Solution*

Potassium dichromate, as previously stated, may be prepared to such a high degree of purity that many authors recommend weighing out the required amount of the salt and making up to volume, without further standardization.

Standardization with 0.1 N Sodium Thiosulphate

Pipette 25 cc of the dichromate solution to be standardized into a 300 cc Erlenmeyer flask. Add 15 cc of 15% KI solution and 7 cc of concentrated HCl. Titrate immediately with thiosulphate, using starch as an indicator. The color change is from blue to the characteristic green of chromic salts. This procedure has been dealt with under the standardization of thiosulphate.

Reaction:



$$\text{Calculations: } N_{\text{K}_2\text{Cr}_2\text{O}_7} \times V_{\text{K}_2\text{Cr}_2\text{O}_7} = N_{\text{Thio}} \times V_{\text{Thio}}$$

Standardization with Ferrous Ammonium Sulphate

Potassium dichromate may also be standardized by use of ferrous ammonium sulphate²² as a primary

²² Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **18**, 759 (1926).

standard. Sufficient amount of the purest obtainable salt is weighed out to give a titration of 35–40 cc. The titration may be carried out with either an outside indicator, potassium ferricyanide, or an internal indicator such as diphenylamine,²³ or diphenylbenzidine.^{24, 25} If ferricyanide is used, a 0.01% solution is spotted on a porcelain plate, the ferrous ammonium sulphate is dissolved in 25 cc of distilled water, 10 cc of dilute H_2SO_4 added; and titrated with potassium dichromate. When the end point is near, the solution is spotted at intervals of 0.1 cc. The end point is reached when no blue color appears on the spot plate after two minutes.

If diphenylamine or diphenylbenzidine is used, it is necessary to add phosphoric acid either at the beginning of the titration or shortly before the true end point is reached. Phosphoric acid is necessary, since if it is not used, the end point is reached too soon, due to the indicator being partially oxidized by ferric ions. Phosphoric acid forms complexes with ferric ions, lowering the oxidation potential of the ferrous-ferric system. An indicator blank should be run, and the titration subtracted from the total titration of the sample.

Dissolve the sample in 25 cc of distilled water, add

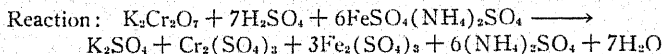
²³ J. Knop, *J. Am. Chem. Soc.* **46**, 263 (1924).

²⁴ H. H. Willard and Philena Young, *J. Ind. Eng. Chem.* **20**, 764 (1928).

²⁵ W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* **49**, 357 (1927).

88 *The Standardization of Volumetric Solutions*

10 cc of dilute H_2SO_4 and 15 cc of sulphuric acid-phosphoric acid mixture (150 cc conc. H_2SO_4 and 160 cc 85% phosphoric acid made up to one liter). Add 2–3 drops of 1% indicator solution (in concentrated H_2SO_4) and titrate. As the end point approaches, the solution turns greenish blue and at the end point suddenly changes to an intense blue color.

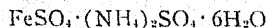


Calculations: The equivalent weight of ferrous ammonium sulphate, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's salt) is 391.90

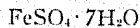
$$\text{Normality} = \frac{\text{Wt. of sample}}{0.3919 \times \text{net cc Titration}}$$

STANDARDIZATION OF FERROUS AMMONIUM SULPHATE, OR FERROUS SULPHATE

Molecular Weight: 391.90
Equivalent Weight: 391.90



Molecular Weight: 278.01
Equivalent Weight: 278.01



Preparation of the Solution

Ferrous ammonium sulphate—Mohr's salt—possesses the advantage of a high equivalent weight and the disadvantage in that it often contains small amounts of impurities. This, in spite of its high reacting weight, prevents it from being an ideal primary standard for oxidimetry. However, with regard to a standard solu-

tion of the salt, this does not present any difficulty, since it is only necessary to weigh slightly more than the theoretical amount to compensate for these impurities.

Mohr's salt and ferrous sulphate are subject to air oxidation, and both effloresce. They should be kept in tightly stoppered bottles. To overcome these difficulties, various methods have been used in preparing the pure salts. Kolthoff ²⁶ suggests using ferric ammonium sulphate and reducing the solution with hydrogen sulphide. The crystallized ferrous ammonium sulphate is dried to constant weight over saturated sodium bromide solution. It is also possible to reduce ferric ammonium sulphate in a Jones reductor just before standardization. Kolthoff ²⁷ states that ferric ammonium sulphate weathers readily but is stable at a relative humidity of 70%. Therefore, if this salt is used as a starting point, it is first necessary to allow it to come to equilibrium at 70% relative humidity.

If the commercial salts are used in the preparation of tenth normal solutions, 40 gm of Mohr's salt or 28 gm of ferrous sulphate are weighed, dissolved in 300 cc of distilled water containing 30 cc of concentrated sulphuric acid, and made up to one liter.

²⁶ F. M. Kolthoff, *Pharm. Weekblad* **61**, 561 (1926).

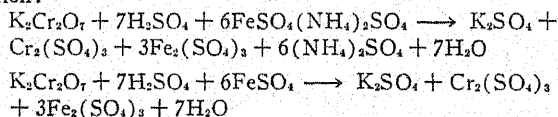
²⁷ Kolthoff and Furman, *Volumetric Analysis, Vol. II* (John Wiley, 1929), 294.

90 *The Standardization of Volumetric Solutions*

Standardization with Tenth Normal Potassium Dichromate

Pipette 25 cc of freshly prepared solution into a 250 cc Erlenmeyer flask. Add 10 cc of dilute sulphuric acid and 15 cc of sulphuric acid-phosphoric acid mixture (150 cc of conc. sulphuric acid, 160 cc of 85% phosphoric acid made up to one liter). Add 2-3 drops of indicator (1% solution of diphenylamine or diphenylbenzidine in concentrated sulphuric acid) and titrate with standard dichromate to the appearance of a deep blue end point. A blank titration should be run on the indicator and subtracted from the total titration.

Reaction:



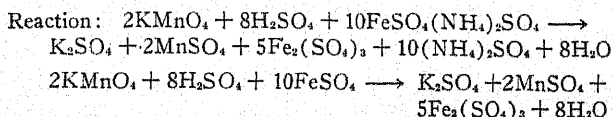
$$\begin{aligned} \text{Calculations: } N_{\text{K}_2\text{Cr}_2\text{O}_7} \times V_{\text{K}_2\text{Cr}_2\text{O}_7} &= N_{\text{Mohr's Salt}} \times V_{\text{Mohr's Salt}} \\ N_{\text{K}_2\text{Cr}_2\text{O}_7} \times V_{\text{K}_2\text{Cr}_2\text{O}_7} &= N_{\text{FeSO}_4} \times V_{\text{FeSO}_4} \end{aligned}$$

Note: The explanation of the use of phosphoric acid is given under the standardization of potassium dichromate.

Standardization with Tenth Normal Potassium Permanganate

Pipette 25 cc of ferrous ammonium sulphate or ferrous sulphate solution into a 250 cc Erlenmeyer flask. Add 25 cc of distilled water, 10 cc of dilute sulphuric acid, and 15 cc of sulphuric acid-phosphoric acid mixture. Titrate with previously standardized

tenth normal permanganate to the appearance of the first permanent pink color.



$$\begin{aligned} \text{Calculations: } N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} &= N_{\text{Mohr's Salt}} \times V_{\text{Mohr's Salt}} \\ N_{\text{KMnO}_4} \times V_{\text{KMnO}_4} &= N_{\text{FeSO}_4} \times V_{\text{FeSO}_4} \end{aligned}$$

STANDARDIZATION OF ARSENIOS OXIDE

Molecular Weight: 197.82
Equivalent Weight: 49.46

As₂O₃

Preparation of the Solution

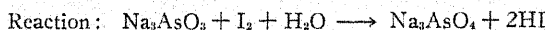
Arsenic trioxide in pure form may be obtained from the Bureau of Standards. Weigh out 4.946 gm of arsenious oxide and dissolve in 250 cc of distilled water, containing 50 cc of normal sodium hydroxide. When solution has taken place, add enough acid, either hydrochloric or sulphuric, until the solution is neutral or faintly acid. Other methods dissolve arsenic trioxide in water containing sodium carbonate. The control of the final pH is important, since if the solution is too alkaline, the arsenite is more or less easily oxidized to arsenate, which naturally affects the titer. Tannanaev²⁸ states, however, that if the pH is kept between 7 and 9, the solution will keep indefinitely.

²⁸ N. A. Tannanaev, *Ukrainskii Khim. Zhurnal* 5, Sci. Pt. 217 (1930); *Chemical Abstracts* 25, 2070 (1931).

92 The Standardization of Volumetric Solutions

Standardization with Iodine

Pipette 25 cc of solution into an Erlenmeyer flask containing 25 cc of distilled water in which 1 gm of sodium bicarbonate has been dissolved. Titrate with standard iodine to the appearance of a blue color, using starch as an indicator. Sodium bicarbonate keeps the pH of the solution at about 8.36.



$$\text{Calculations: } N_{\text{As}_2\text{O}_3} \times V_{\text{As}_2\text{O}_3} = N_{\text{I}_2} \times V_{\text{I}_2}$$

STANDARDIZATION OF POTASSIUM BROMATE

Molecular Weight: 167.02

KBrO₃

Equivalent Weight: 27.84

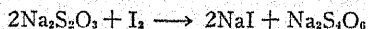
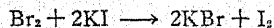
Preparation of the Solution

Weigh out 2.784 gm of potassium bromate, previously dried at 150° C, dissolve in a small quantity of distilled water, and dilute to one liter.

Standardization with 0.1 N Sodium Thiosulphate

Pipette 25 cc of the bromate solution into a glass-stoppered bottle or iodine flask and add 20 cc of 10% sulphuric acid saturated with potassium bromide. Restopper the flask quickly and let stand for two minutes. Now add 5 cc of saturated potassium iodide solution, let stand one minute and titrate with N/10 sodium thiosulphate, using starch as an indicator.

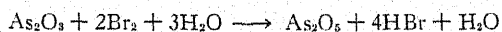
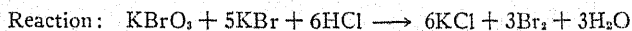
Reactions:



$$\text{Calculations: } N_{\text{KBrO}_3} \times V_{\text{KBrO}_3} = N_{\text{Thio}} \times V_{\text{Thio}}$$

Standardization with Arsenious Acid

Pipette 25 cc of standard arsenious oxide into a 300 cc Erlenmeyer flask, add 30 cc of 1:1 hydrochloric acid and 0.5 gm of potassium bromide. Add 1-2 drops of methyl orange. Titrate with the bromate solution, constantly agitating the flask. The end point is approached slowly. The color change is from red to colorless or pale yellow. The indicator change is due to bleaching of the compound by free bromine.

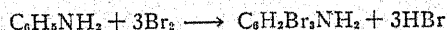


$$\text{Calculations: } N_{\text{KBrO}_3} \times V_{\text{KBrO}_3} = N_{\text{As}_2\text{O}_3} \times V_{\text{As}_2\text{O}_3}$$

Standardization with Aniline

Aniline may be used as a standard for potassium bromate. Its reaction is similar to phenol, in that it forms a tri-brom compound. An appropriate quantity of freshly distilled aniline is weighed out and transferred to a glass-stoppered iodine flask containing 20 cc of 10% sulphuric acid saturated with potassium bromide. Add 50 cc of bromate solution, and let stand for five minutes. Now add 5 cc of saturated potassium iodide solution, let stand one minute, and titrate the iodine with sodium thiosulphate, using starch as an indicator.

Reaction:



94 *The Standardization of Volumetric Solutions*

Calculations: The equivalent weight of aniline is 15.50

$$\text{Normality} = \frac{\text{Wt. of aniline}}{0.0155 \times \text{net cc of KBrO}_3}$$

Note: Potassium bromate solution is sometimes made up with potassium bromide. In this case, 50 gm of bromide are added per liter.

STANDARDIZATION OF POTASSIUM IODATE

Molecular Weight: 214.03

KIO₃

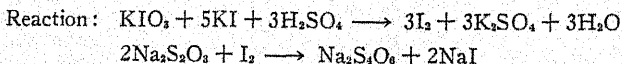
Equivalent Weight: 35.67

Preparation of the Solution

Potassium iodate may be obtained pure by recrystallization from water. After drying at 180° C, the exact equivalent weight may be accurately weighed out, and made up to volume. However, to avoid any uncertainty as to the purity of the potassium iodate, it is best to standardize the solution.

Standardization with Sodium Thiosulphate

Pipette 25 cc of potassium iodate into a glass-stoppered flask containing 20 cc of 10% sulphuric acid and 5 cc of saturated potassium iodide solution. The reaction proceeds rapidly, and the solution may be titrated, immediately, with standard thiosulphate solution, using starch as an indicator.

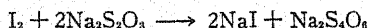
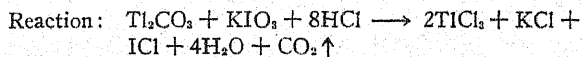


$$\text{Calculations: } N_{\text{KIO}_3} \times V_{\text{KIO}_3} = N_{\text{Thio}} \times V_{\text{Thio}}$$

Standardization with Thallous Carbonate

Berry²⁹ has suggested the use of thallous carbonate as a primary standard for iodate solutions.

Weigh out 0.4–0.5 gm of the salt, dissolve in distilled water, and make strongly acid with concentrated HCl. Add 15 cc of saturated KI solution, and titrate the liberated iodine, using starch as an indicator.



Calculations: The equivalent weight of Ti_2CO_3 is 117.2

$$\text{Normality} = \frac{\text{Wt. Ti}_2\text{CO}_3}{0.1172 \times \text{cc Titration}}$$

STANDARDIZATION OF CERIC SULPHATE

Molecular Weight: 332.25

$\text{Ce}(\text{SO}_4)_2$

Equivalent Weight: 332.25

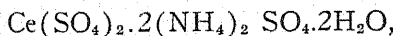
Ceric sulphate is a powerful oxidizing agent, and has been offered as a substitute for permanganate in oxidation reactions. There are numerous advantages, chief among which is the comparative stability³⁰ of ceric sulphate solutions and the fact that there is no decomposition when oxidations with excess sulphate are carried out at boiling temperatures.

Ceric sulphate, as received from chemical supply

²⁹ A. J. Berry, *Analyst* 64, 27 (1939).

³⁰ N. H. Furman, *J. Am. Chem. Soc.* 50, 755 (1928).

houses, averages around 50% as ceric sulphate, the variation being due to the presence of rare earths as impurities, and the fact that the salt is not completely anhydrous. Ceric ammonium sulphate,



whose purity is around 80%, is also used in place of anhydrous ceric sulphate.

Preparation of the Solution

Allowing the ceric sulphate to be 50%, weigh out a little more than twice the equivalent weight, or 67 gm for a tenth normal solution. Add 100 cc of water and 30 cc of concentrated H_2SO_4 . Let the solution stand until the salt is dissolved, adding more water or heating, if necessary. Make up to one liter. The solution will be approximately tenth normal in ceric sulphate and one normal in sulphuric acid.

If ceric ammonium sulphate ($2\text{H}_2\text{O}$) is used, weigh out an equivalent quantity of the salt, depending upon its purity, and dissolve in the same manner as for ceric sulphate. Standard solutions of ceric sulphate may also be prepared by dissolving the oxide, CeO_2 ,³¹ in dilute sulphuric acid.

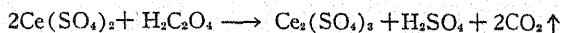
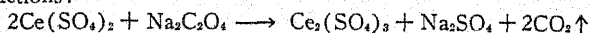
Standardisation with Oxalic Acid or Sodium Oxalate

Weigh out 0.25–0.30 gm of oxalate and dissolve in 100 cc of distilled water. Add 10 cc of 1:1 H_2SO_4 . Heat to 90–95° C and titrate with the ceric sulphate

³¹ H. H. Willard and Philena Young, *J. Am. Chem. Soc.*, 50, 1322 (1928).

solution. The solution may be titrated using the ceric sulphate as an indicator, the end point being taken as the first permanent yellow tinge. Orthoferrous-phenanthroline^{32, 33, 34, 35} is a very satisfactory indicator. One drop of the indicator solution is added. The color change is from pink to blue.

Reactions:



$$\text{Calculations: Normality} = \frac{\text{Wt. of oxalate}}{0.067 \times \text{cc Titration}} \quad \text{or}$$

$$\text{Normality} = \frac{\text{Wt. of oxalic acid}}{0.06303 \times \text{cc Titration}}$$

Standardization with Arsenious Oxide

Either a standard solution of tenth normal arsenite or pure arsenic trioxide (obtainable from the Bureau of Standards) may be used. If the dry salt is used, weigh 0.20 gm samples and dissolve in a few cubic centimeters of normal sodium hydroxide. If a previously standardized solution of arsenite is used, pipette

³² G. H. Walden, L. P. Hammett, and R. P. Chapman, *J. Am. Chem. Soc.* **53**, 3908 (1931).

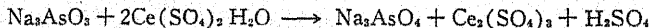
³³ Monograph, Ortho-phenanthroline, published by The G. Frederick Smith Chemical Co., 857 McKinley Ave., Columbus, Ohio, P. O. Box 2611, Station D.

³⁴ A. U. Kirsanov and U. M. Cherkasov, *Zavodskaya Lab.* **5**, 143; *Bull. Soc. Chem.* (5), **3**, 817; *Chemical Abstracts* **30**, 4779 (1936).

³⁵ H. H. Willard and Philena Young, *J. Am. Chem. Soc.* **55**, 3260 (1933).

25 cc into an Erlenmeyer flask. Either sulphuric or hydrochloric acid may be added. The solution must be strongly acid, otherwise cerous sulphate will precipitate, since it is not very soluble in dilute acid. Add 50–75 cc of distilled water and 20–25 cc of concentrated hydrochloric acid or an equivalent amount of sulphuric acid. If the reagent itself is used as the indicator, the solution, as previously stated, must be heated to around 100° C, since the intensity of color is much greater when hot, making the end point easier to observe. Also, in the absence of a catalyst such as iodine monochloride³⁶ or osmium tetroxide, the solution must be heated to promote a fast reaction. Ortho-phenanthroline ferrous complex may be used as an indicator, one drop of a 0.025% solution being sufficient.

Reaction:



$$\text{Calculations: Normality} = \frac{\text{Wt. of As}_2\text{O}_3}{0.04946 \times \text{cc Titration}}$$

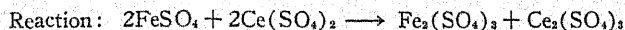
$$\text{or } N_{\text{Ce}(\text{SO}_4)_2} \times V_{\text{Ce}(\text{SO}_4)_2} = N_{\text{As}_2\text{O}_3} \times V_{\text{As}_2\text{O}_3}$$

Standardization with Mohr's Salt or Ferrous Sulphate

Make an approximately tenth normal solution of either Mohr's salt or ferrous sulphate, and determine its strength by titration with a standard solution of potassium dichromate. This is necessary, since the composition of either salt cannot be depended upon.

³⁶ E. H. Swift and C. H. Gregory, *J. Am. Chem. Soc.* 52, 901 (1930).

Having determined the exact strength of the iron solution, pipette 25 cc into an Erlenmeyer flask, and make the volume up to 100 cc. Add 10 cc of 1:1 sulphuric acid, and titrate with ceric sulphate, using ortho-phenanthroline ferrous complex.



Calculations: $N_{\text{Ce}(\text{SO}_4)_2} \times V_{\text{Ce}(\text{SO}_4)_2} = N_{\text{FeSO}_4} \times V_{\text{FeSO}_4}$

SUPPLEMENTARY REFERENCES

Potassium Dichromate as a Standard in Iodimetry and the Determination of Chromates by the Iodide Method, W. C. Vosburgh, *J. Am. Chem. Soc.* **44**, 2120 (1922).

Standardization of Solutions Used in Iodimetry I, S. Popoff and F. L. Chambers, *J. Am. Chem. Soc.* **45**, 1358 (1923).

Standardization of Solutions Used in Iodimetry II, S. Popoff and J. L. Whitman, *J. Am. Chem. Soc.* **47**, 2259 (1925).

Applications of Ceric Sulphate in Volumetric Analysis IX. The Standardization of Thiosulphate Solutions, N. H. Furman and J. H. Wallace, *J. Am. Chem. Soc.* **53**, 1283 (1931).

Employment of Potassium Ferrocyanide in Standardization of Dilute Potassium Permanganate, E. J. deBeer and Axel M. Hjort, *J. Ind. Eng. Chem., Anal. Ed.* **7**, 120 (1935).

The Preparation and Preservation of Standard Potassium Permanganate Solution, Takio Kato, *J. Chem. Soc. Japan* **48**, 408 (1927); *Chemical Abstracts* **22**, 1932 (1928).

The use of Bromate in Titrations with Special Reference to the Indicator Question, Oscar Collenburg, *Tids. Kjemi Bergvesen* **5**, 220, 239 (1925); *Chemical Abstracts* **20**, 883 (1925).

The Preparation of Standard Solutions of Potassium Bromate, Morris L. Yakowitz, *J. Assoc. Official Agr. Chem.* **18**, 505 (1935).

Analysis of Feldspar, Method for Determining Normalities of Potassium Bromate and Sodium Thiosulphate in the Knowles-Redmond Volumetric Procedure for Alumina, E. W. Koenig, *J. Am. Ceram. Soc.* **19**, 257 (1936).

Volumetric Iodate Methods, Jamieson, Chemical Catalog Co.

Use of Indicators, H. H. Willard and Philena Young, *J. Am. Chem. Soc.* **55**, 3260 (1933).

Preparation and Stability of Solutions IX, H. H. Willard and Philena Young, *J. Am. Chem. Soc.* **51**, 149 (1929).

Experiments on Quantitative Oxidation with Ceric Sulphate, A. J. Berry, *Analyst*, August (1929).

CHAPTER VIII

Miscellaneous Standard Solutions

UNDER this heading are grouped several solutions whose practical importance in the analytical laboratory—with the exception of Wijs and Hanus solutions—is slight. However, since they are used to some extent, they have been included in the list of standard solutions.

STANDARDIZATION OF WIJS' OR HANUS' SOLUTION

Both of these solutions are used to determine unsaturation in organic compounds. The active constituent of Wijs' solution is iodine monochloride, and that of Hanus' solution is iodine monobromide. Glacial acetic acid is used as the solvent. There is no necessity for the solutions to contain exact equivalents.

Preparation of the Solution

Weigh out approximately 12.7 gm of iodine, and dissolve in several hundred cubic centimeters of glacial acetic acid. The iodine will dissolve readily in the acetic acid, if it has been ground to a fine powder in a

mortar. Gentle heating in a covered flask will facilitate solution, but prolonged heating will result in an appreciable loss of iodine. When the iodine is in complete solution, an equivalent (approximately) of chlorine or bromine is added. In the case of Wijs' solution, chlorine is bubbled slowly into the solution until the color begins to change and becomes definitely lighter. Caution: iodine must always be in excess, and the final color should be a deep red brown. A little experience will dictate the approximate point at which to stop.

Hanus' solution is prepared by adding 6.6 cc of bromine (not bromine water) to the acetic acid solution of iodine. Both solutions are now approximately 0.2 normal with respect to the iodine, since iodine, chlorine, and bromine are all equivalent to each other. Keep the solutions in brown bottles and store in a cupboard. Even under these conditions, the solutions will change their titer.

Standardization of the Solution

It is not necessary to standardize the solution, but its strength in terms of tenth normal thiosulphate is usually determined.

Pipette 25 cc of either Wijs' or Hanus' solution into a 250 cc Erlenmeyer flask, add 15 cc of 15% potassium iodide, and titrate with thiosulphate, using starch as an indicator, to the disappearance of the blue color. Record this titer as the strength of the solution. In running determinations of iodine values, it is always

necessary to include a blank, since, as stated above, the titer will change over a period of time.

STANDARDIZATION OF IODINE THIOCYANATE SOLUTION

Iodine thiocyanate is also used to determine unsaturation in organic compounds. The solution is stable for a comparatively short time, and should be kept in the dark.

Preparation of the Solution

To 900 cc of C.P. benzol, add 50 cc of acetic anhydride and 50 cc of glacial acetic acid. Allow to stand in a dry, glass-stoppered bottle, in the dark for eight days. Add 15 gm of lead thiocyanate and 2 cc of liquid bromine. Shake vigorously, at frequent intervals, until the solution has become decolorized. During this period, keep the solution in the dark or away from any source of bright light. After the solution is decolorized, add 4-6 gm of iodine. As soon as the iodine dissolves, filter the solution rapidly into a dry, glass-stoppered bottle and store in the dark.

Standardization of the Solution

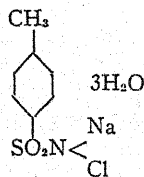
The strength of the solution is determined by titration with tenth normal thiosulphate.

Pipette 25 cc of the solution into a glass-stoppered iodine flask. Add quickly 15 cc of 15% potassium iodide, shake vigorously, and titrate the liberated iodine with tenth normal thiosulphate, using starch as an

indicator. A blank determination must always be run when determining unsaturation.

STANDARDIZATION OF CHLORAMINE T

Molecular Weight: 281.5
Equivalent Weight: 140.75



Chloramine T—tolamine, activin—is the sodium salt of p-toluene sulphonchloroamide. Its use as a volumetric reagent ^{1, 2, 3, 4} was suggested by Noll.^{5, 6} In its action, chloramine T resembles the hypochlorites and reacts in oxidation reactions similar to iodine. It has been used in determination of sulphites, arsenic, antimony, tin, and iron.

¹ E. Jungmichl and J. Hackl, *Melliand Textilber.* 7, 850 (1926).

² O. Tomicek and B. Sucharda, *Casopis Ceskoslov. Lekarnictva* 11, 285, 309 (1931); *Chemical Abstracts* 26, 1210 (1932).

³ M. Markees, *Pharm. Acta Helv.* 6, 106 (1931).

⁴ A. S. Komarovskii, Vera Feodorovna Filanova, and I. M. Korenman, *J. Applied Chem. (U.S.S.R.)* 6, 742 (1933); *Z. Anal. Chem.* 96, 321 (1934).

⁵ A. Noll, *Papier Fabr. Tech. Wiss. Teil* 22, 385; *Zellstoff u. Papier* 4, 218 (1924); *Chemical Abstracts* 19, 176 (1925).

⁶ A. Noll, *Chem. Ztg.* 48, 845 (1924).

Preparation of the Solution

Since the purity of the commercial product may vary, approximately 15 gm are dissolved in water and made up to one liter (actually 14.1 gm represent one equivalent). If there are any doubts as to the purity, the salt may be recrystallized from water. The solution is stable,^{7,8} if kept in brown bottles.

Standardization with Arsenious Acid

Standardization may be made either with the dry salt or with a previously standardized solution of arsenious acid. Pipette 25 cc of tenth normal arsenious acid into an Erlenmeyer flask. Add 2-3 cc of a 10% solution of potassium iodide (or a small crystal), 5 cc of starch solution, and titrate to the first appearance of a blue color.

$$\begin{aligned} \text{Calculations: } N_{\text{Chlor.}} \times V_{\text{Chlor.}} &= N_{\text{As}_2\text{O}_3} \times V_{\text{As}_2\text{O}_3} \\ \text{or } \text{Normality} &= \frac{\text{Wt. of As}_2\text{O}_3}{0.04946 \times \text{cc Titration}} \end{aligned}$$

STANDARDIZATION OF HYPOCHLORITE SOLUTIONS

Hypochlorites and hypobromites are powerful oxidizing agents and useful in oxidation reactions that are carried out in alkaline or neutral solution. Kolthoff and Stenger⁹ have proposed the use of calcium hypo-

⁷ Julius Bebie, *J. Am. Pharm. Assoc.* 9, 974 (1920).

⁸ Bernard Salkin, *J. Am. Pharm. Assoc.* 13, 613 (1924).

⁹ I. M. Kolthoff and V. A. Stenger, *Ind. Eng. Chem., Anal. Ed.* 7, 79 (1935).

chlorite as a standard reagent, since this compound is much more stable than the alkali hypochlorites. It may be obtained from the Mathieson Alkali Co., 60 East 42nd Street, New York City, under the code letters CCH.

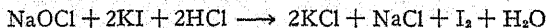
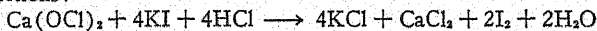
Preparation of the Solution

Determine the available chlorine in the sample and weigh out enough to make a tenth normal solution when diluted to one liter. Store in a brown bottle, tightly stoppered. It will be necessary to recheck the titer of the solution, particularly if considerable time has elapsed since the solution was last used.

Standardization with Sodium Thiosulphate

Pipette 25 cc of the hypochlorite into an Erlenmeyer flask, and add 15 cc of a 15% solution of potassium iodide. Make up the volume to approximately 100 cc with distilled water, add 10 cc of concentrated hydrochloric acid, and titrate with thiosulphate to the disappearance of the blue color, using starch as an indicator.

Reactions:



Equivalent weight in either case: $\frac{\text{Mol. Wt.}}{2}$

$$\text{Calculations: } N_{\text{OCl}} \times V_{\text{OCl}} = N_{\text{Thio}} \times V_{\text{Thio}}$$

Standardization with Arsenious Acid

Pipette 25 cc of the hypochlorite solution into a

250 cc Erlenmeyer flask. Add 50 cc of a tenth normal solution of arsenious acid. Titrate the excess arsenious acid with tenth normal iodine to the appearance of the blue starch-iodine color.

Calculations: Calculate the net cubic centimeters of arsenious acid used,
then,

$$N_{\text{OCl}} \times V_{\text{OCl}} = N_{\text{As}_2\text{O}_3} \times V_{\text{As}_2\text{O}_3}$$

A more recent addition to this type of standard oxidizing solution is the use of sodium chlorite as a volumetric oxidizing agent. Jackson and Parsons¹⁰ have prepared and used it successfully for the determination of sulphurous acid and sulphites.

STANDARDIZATION OF SODIUM CHLORITE

Molecular Weight: 90.454
Equivalent Weight: 22.614

NaClO2

Preparation of the Solution

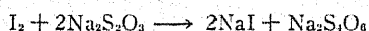
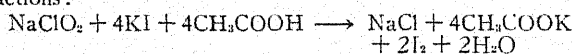
Sodium chlorite is obtainable as a white crystalline solid, very soluble in water, slightly hygroscopic, and about 98% pure, the impurities consisting of sodium chloride, sodium chlorate, and water. The solution is stable over a period of several months, if kept in the dark. Weigh out the required amount of the salt, dissolve in distilled water, and make up to volume.

¹⁰ D. T. Jackson and J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.* 9, 14 (1937).

Standardization with Sodium Thiosulphate

Pipette 25 cc of the solution into an Erlenmeyer flask containing 75 cc of distilled water, 15 cc of 10% KI and 15 cc of 30% acetic acid. Titrate the liberated iodine with previously standardized thiosulphate solution, using starch as an indicator.

Reactions:



STANDARDIZATION OF TITANIUM TRICHLORIDE OR SULPHATE

Molecular Weight: 154.27

 TiCl_3

Equivalent Weight: 154.27

Molecular Weight: 383.98

 $\text{Ti}_2(\text{SO}_4)_3$

Equivalent Weight: 383.98

Titanous salts are powerful reducing agents. As they are affected by air, the solutions are relatively unstable and must be kept under some inert gas. This necessitates special apparatus.¹¹ For isolated analyses, titanous solutions are not recommended. They find their usefulness, however, in routine work, where numerous determinations of the same sort are being run daily.

Preparation of the Solution

Concentrated solutions of the salts may be purchased.

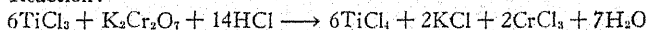
¹¹ W. M. Thornton, Jr. and A. E. Ward, *J. Ind. Eng. Chem.* 19, 150 (1927).

From the strength of the solution, the volume which will contain an equivalent weight can be calculated. This is diluted with freshly boiled distilled water containing three per cent of concentrated hydrochloric acid (or equivalent of conc. H_2SO_4).

*Standardization with Potassium Dichromate*¹¹

Pipette 25 cc of tenth normal dichromate into a 250 cc Erlenmeyer flask containing 50 cc of boiled distilled water and 5 cc of concentrated hydrochloric acid. Add several drops of diphenylamine as an indicator. Bubble carbon dioxide through the solution continuously and titrate with the titanous solution to an end point.

Reaction:



$$\text{Calculations: } N_{\text{TiCl}_3} \times V_{\text{TiCl}_3} = N_{\text{K}_2\text{Cr}_2\text{O}_7} \times V_{\text{K}_2\text{Cr}_2\text{O}_7}$$

If the dry salt was used, then,

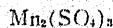
$$\text{Normality} = \frac{\text{Wt. of } \text{K}_2\text{Cr}_2\text{O}_7}{0.04903 \times \text{cc Titration}}$$

Equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7 = 49.03$

Note: The solution may also be standardized by titrating a sample of ferric ammonium sulphate (ferric alum), using 10 cc of 15% potassium thiocyanate as an indicator and titrating to the disappearance of the red ferric thiocyanate color. Follow the general directions as outlined under *Standardization*.

STANDARDIZATION OF MANGANIC SULPHATE

Molecular Weight: 398.04



Equivalent Weight: 398.04

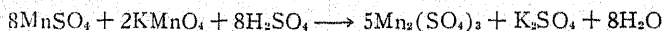
The use of manganic sulphate¹² as a standard re-

¹² A. R. Ubbelohde, *J. Chem. Soc.* 1605 (1935).

agent, in place of permanganate, presents interesting possibilities. Certain difficulties attendant to permanganate titration, such as the presence of chlorides, are overcome by manganic sulphate. A. R. Ubbelohde¹² states that satisfactory results have been obtained in the estimation of nitrites, oxalates, vanadium salts and hydrogen peroxide, and that rapid and satisfactory end points can be obtained without difficulty in the presence of chlorides.

Preparation of the Solution

According to Ubbelohde, a tenth normal solution may be prepared from manganous sulphate in the following manner, and according to the equation:

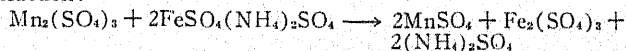


Dissolve 15.10 gm of manganous sulphate in 6 *N* H_2SO_4 , and make up to a liter with 6 *N* H_2SO_4 , keeping the solution cool. Now add 12 cc of *N*/2 KMnO_4 , 2 cc at a time, at intervals of three minutes. A further 2 cc of concentrated H_2SO_4 were added after 8 cc and 12 cc of the KMnO_4 solution, and the solution stored four hours in the dark before use. With these precautions, the reaction proceeds smoothly. If larger volumes are required, special precautions must be taken for cooling the solution to prevent formation of precipitates of the higher oxides. This solution is stable at room temperature, but on dilution, unless the acid concentration is increased, hydrolysis will take place.

Standardization with Ferrous Ammonium Sulphate

Weigh out the necessary amount of ferrous ammonium sulphate and dissolve in 25 cc of distilled water. Add 10 cc of dilute H_2SO_4 and titrate. One drop excess of the reagent gives a definite pink color, which is greatly improved by addition of two drops of glacial phosphoric acid.

Reaction:



$$\text{Calculations: Normality} = \frac{\text{Wt. of } \text{FeSO}_4(\text{NH}_4)_2\text{SO}_4}{0.39804 \times \text{cc Titration}}$$

SUPPLEMENTARY REFERENCES

Calcium Chlorite as a Volumetric Oxidizing Agent, G. R. Levi, *Ind. Eng. Chem., Anal. Ed.* **9**, 250 (1937).

See also J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.* **9**, 250 (1937).

Oxidation of Amino Acids and of Related Substances with Chloramine, T. D. Dakin, *Biochem. J.* **11**, 79 (1917).

Chloramine, P. N. Van Eck, *Pharm. Weekblad* **63**, 1117 (1926).

Oxidizing Action of Chloramine, T. G. Schiemann and P. Novak, *Z. Angew. Chem.* **40**, 1032 (1927).

The Oxidizing Power of Chloramines, J. Koetschet, P. Koetschet, and Pierre Viaud, *Helv. Chem. Acta* **13**, 587 (1930).

Calcium Chlorite as a Volumetric Oxidizing Agent, G. R. Levi, *Ind. Eng. Chem., Anal. Ed.* **9**, 250 (1937).

J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.* **9**, 250 (1937).

Electrometric Standardization of Titanous Solution, W. S. Hendrixson and L. M. Verbeck, *J. Am. Chem. Soc.* **44**, 2382 (1922).

Standardizing Titanous Chloride Solutions and Potentiometric Titration of Copper, E. Zintl and A. Rauch, *Z. Anorg. Allgem. Chem.* **146**, 281 (1925).

Application of Titanous Chloride to Potentiometric Titrations, I. M. Kolthoff and O. Tomicek, *Rec. Trav. Chem.* **43**, 768 (1924).

Applied Inorganic Analysis, Hillebrand and Lundell (1929), 308.

Stock Solutions of Indicators

ACID-BASE

Phenolphthalein: One gram dissolved in one liter of 50% alcohol. Alcohol is always faintly acid and must be first neutralized with 0.1N caustic before adding the indicator.

Methyl Orange: One gram dissolved in one liter of distilled water.

Methyl Yellow: 0.1% in alcohol.

Methyl Red: 0.1% in alcohol.

Thymol Blue: 0.1% in alcohol.

OXIDATION-REDUCTION

Diphenylamine: 1% in conc. H_2SO_4 .

Diphenylbenzidine: 1% in conc. H_2SO_4 .

Ferrous *o*-phenanthroline: can be purchased* ready for use.

*The G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio. P.O.B. 2611—Station D.

PRECIPITATION

Ferric Ammonium Sulphate: Saturated solution in water. Enough concentrated HNO_3 added to clear the solution.

Ferric Nitrate: 10% solution in water.

Potassium Chromate: 5% solution in water.

Uranyl Acetate: 1% solution in water.

STOCK SOLUTIONS OF LABORATORY REAGENTS

Concentrated Acids

Sulphuric acid	— 36 Normal
Hydrochloric acid	— 12 Normal
Nitric acid	— 16 Normal
Acetic acid	— 17.5 Normal
Hydrofluoric acid	— 48%
Aqua regia	— Mix 3 vols. of conc. HCl and 1 vol. conc. HNO_3 just before using.

Dilute Acids

Sulphuric acid	— 18 Normal. Dilute 460 cc of concentrated acid with 540 cc of distilled water.
Sulphuric acid	— 6 Normal. Dilute 1 vol. of concentrated acid with 5 vols. of distilled water.
Hydrochloric acid	— 6 Normal. Mix equal volumes of concentrated acid and distilled water.

114 *The Standardization of Volumetric Solutions*

- Nitric acid — 6 Normal. Dilute 380 cc of concentrated acid with 620 cc of distilled water.
- Perchloric acid — 2 Normal. Dilute 220 cc of 60% acid with 780 cc of distilled water.
- Acetic acid — 6 Normal. Dilute 350 cc of glacial acetic acid to one liter with distilled water.

Bases

- Ammonium hydroxide — 15 Normal. Concentrated.
6 Normal. Dilute 400 cc of concentrated ammonia with 600 cc of distilled water.
- Sodium hydroxide — 35%. Dissolve one pound of pellet caustic in 748 cc of distilled water.
- Sodium hydroxide — 5 Normal. Dissolve 220 gm in distilled water and make up to one liter.
- Potassium hydroxide — 5 Normal. Contains 312 gm per liter.

Miscellaneous Solutions

- Ammonium chloride — 5 Normal. Contains 268 gm per liter.
- Ammonium nitrate — Normal. Contains 80 gm per liter.

Ammonium oxalate	— 0.5 Normal. Contains 36 gm per liter.
Barium chloride	— 10%. 100 gm dissolved in 900 cc of distilled water.
Picric acid	— Saturated solution in distilled water.
Potassium iodide	— 15%. 150 gm dissolved in 850 cc of distilled water.
Silver nitrate	— 10%. 100 gm dissolved in 900 cc of distilled water.
Sodium carbonate	— 3 Normal. 159 gm per liter.
Stannous chloride	— Normal. 113 gm of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ per liter. The solution is made acid by addition of a few cubic centimeters of conc. HCl. To keep the solution reduced, strips of metallic tin should be added.

NORMAL SOLUTIONS OF ACIDS AND BASES

Compound	Formula	Molecular Weight	Normal Solution Contains gm/l	Milli-Equivalent gm/cc
Acetic Acid	CH_3COOH	60.03	60.03	0.06003
Boric Acid	H_3BO_3	61.84	61.84	0.06184
Hydrobromic Acid	HBr	80.92	80.92	0.08092
Hydrochloric Acid	HCl	36.46	36.46	0.03646
Oxalic Acid	$\text{H}_2\text{C}_2\text{O}_4$	126.05	53.03	0.05303
Phosphoric Acid	H_3PO_4	98.04	32.68	0.04902
Sulphuric Acid	H_2SO_4	98.08	49.04	0.04904
Ammonium Hydroxide	NH_4OH	17.03	17.03	0.01703
Barium Hydroxide	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	315.50	157.75	0.15775
Calcium Hydroxide	$\text{Ca}(\text{OH})_2$	74.09	37.05	0.03705
Potassium Hydroxide	KOH	56.1	56.1	0.0561
Potassium Carbonate	K_2CO_3	138.20	69.10	0.06910
Sodium Carbonate	Na_2CO_3	106.00	53.00	0.05300
Sodium Hydroxide	NaOH	40.00	40.00	0.04000
Sodium Tetraborate	$\text{Na}_2\text{B}_4\text{O}_7$	201.43	100.72	0.10072
Sodium Tetraborate (Hydrated)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	381.43	190.72	0.19072

NORMAL SOLUTIONS OF OXIDIZING AND REDUCING AGENTS

Compound	Formula	Molecular Weight	Normal Solution Contains gm/l	Milli-Equivalent gm/cc
Ammonium Oxalate	$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	142.09	71.05	0.07105
Arsenious Acid	H_3AsO_3	125.93	62.97	0.06297
Arsenious Oxide	As_2O_3	197.82	49.46	0.04946
Bromine	Br	79.916	79.916	0.07992
Calcium Hypochlorite	$\text{Ca}(\text{OCl})_2$	126.99	63.50	0.06350
Chlorine	Cl	35.457	35.457	0.03546
Ferrous Sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278.02	278.02	0.27802
Ferrous Ammonium Sulphate	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	392.14	392.14	0.39214
Hydrogen Peroxide	H_2O_2	34.02	17.01	0.01701
Hydrogen Sulphide	H_2S	34.08	17.04	0.01704
Iodine	I	126.92	126.92	0.12692
Oxalic Acid	$\text{H}_2\text{C}_2\text{O}_4$	90.036	45.018	0.04502
Oxalic Acid (Hydrated)	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	126.05	63.03	0.06303
Potassium Bromate	KBrO_3	167.02	27.84	0.02784
Potassium Dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	294.21	49.04	0.04904
Potassium Iodate	KIO_3	214.03	35.67	0.03567
Potassium Permanganate	KMnO_4	158.03	31.61	0.03161
Sodium Thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3$	158.11	158.11	0.15811
Sodium Thiosulphate (Hydrated)	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	248.19	248.19	0.24819
Sodium Oxalate	$\text{Na}_2\text{C}_2\text{O}_4$	133.99	66.995	0.067
Stannous Chloride	SnCl_2	189.61	94.80	0.0948
Stannous Chloride (Hydrated)	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	225.65	112.83	0.11283

NORMAL SOLUTIONS OF PRECIPITATING AGENTS

Compound	Formula	Molecular Weight	Normal Solution Contains gm/l	Milli-Equivalent gm/cc
Ammonium Thiocyanate	NH_4SCN	76.11	76.11	0.07611
Hydrochloric Acid	HCl	36.46	36.46	0.03646
Potassium Ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6$	368.26	368.26	0.36826
Potassium Ferrocyanide (hydrated)	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	422.33	422.33	0.42233
Potassium Thiocyanate	KSCN	97.17	97.17	0.09717
Silver Nitrate	AgNO_3	169.89	169.89	0.16989
Sodium Chloride	NaCl	58.45	58.45	0.05845

PRIMARY STANDARDS

ACID-BASE

The weights of primary standards in the following tables are based on a titration of 40 cc of 0.1 *N* solution.

Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for <i>N</i> /10 Solutions
Guanidine Carbonate	Acid	180.18	0.09009	0.3604
Potassium Bicarbonate	Acid	100.11	0.10011	0.4004
Silver Chloride	HCl	143.34	0.14334	*
Sodium Carbonate	Acid	106.00	0.05300	0.2120
Sodium Tetraborate	Acid	201.43	0.10072	0.4029
Sodium Tetraborate (decahydrate)	Acid	381.43	0.19072	0.7629
Thallous Carbonate	Acid	468.79	0.23440	0.9376
Adipic Acid	Bases	146.14	0.07307	0.2923
Ammonium Acid Sulphate		115.11	0.11511	0.4604
Ammonium Triiodate		544.82	0.27241	1.0896
Benzoic Acid		122.12	0.12212	0.4885
Boric Acid		61.84	0.02061	0.0824
Mercuric Oxide		232.61	0.11630	0.4652
Oxalic Acid		126.05	0.05303	0.2121
Potassium Acid Phthalate		204.06	0.20406	0.8162
Potassium Biiodate		389.85	0.38985	1.5594
Salicylic Acid		138.12	0.06906	0.2762
Sodium Acid Phthalate		189.13	0.18913	0.7565
Succinic Acid		118.09	0.05905	0.2362
Sulfamic Acid		97.49	0.09749	0.3900

* Excess AgNO₃ solution.

OXIDATION-REDUCTION

Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for N/10 Solutions
Ammonium Oxalate (monohydrate)	Permanganate Ceric Sulphate	142.09	0.07106	0.2842
Aniline	Potassium Bromate	93.12	0.01552	0.0621
Arsenious Oxide	Iodine Permanganate Ceric Sulphate	197.82	0.04946	0.1978
Calcium Oxalate	Permanganate Ceric Sulphate	128.08	0.06404	0.2562
Copper	Thiosulphate	63.57	0.06357	0.2543
Copper Oxide	Thiosulphate	79.57	0.07957	0.3183
Copper Sulphate	Thiosulphate	160.63	0.16063	0.6425
	Titanous Chloride			
	Titanous Sulphate			
Ferrous Ammonium Sulphate	Dichromate	391.90	0.39190	1.5676
Ferrous Sulphate (heptahydrate)	Permanganate Dichromate	278.01	0.27801	1.1120
Hydrazine Sulphate	Iodine	130.12	0.03251	0.1300
Iodine	Arsenious Acid Thiosulphate	126.96	0.12692	0.5077
Iron	Permanganate	55.84	0.05584	0.2234
Oxalic Acid (dihydrate)	Permanganate	126.05	0.06303	0.2521
Potassium Biiodate	Thiosulphate	389.95	0.03249	0.1300
Potassium Bromate	Thiosulphate	167.02	0.02784	0.1114
Potassium Dichromate	Thiosulphate	291.21	0.04904	0.1962
	Titanous Chloride			
	Titanous Sulphate			
	Ferrous Ammonium Sulphate			
	Ferrous Sulphate			
Potassium Ferricyanide	Titanous Solutions	329.19	0.32919	1.3168

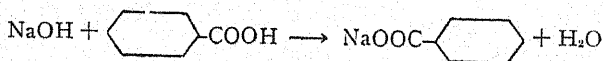
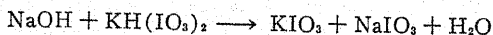
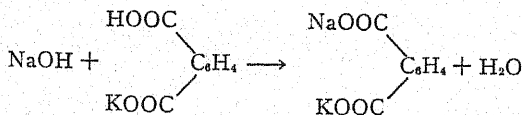
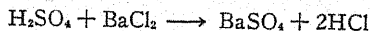
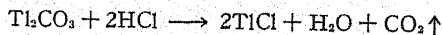
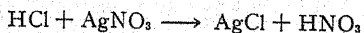
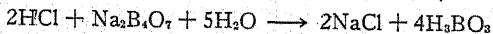
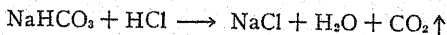
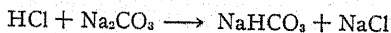
Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for N/10 Solutions
Potassium Ferrocyanide (trihydrate)	Permanganate	422.33	0.42233	1.6893
Potassium Iodate	Thiosulphate	214.03	0.03567	0.1427
Potassium Iodide	Thiosulphate	166.02	0.08301	0.3320
	Permanganate			
	Ceric Sulphate			
Potassium Oxalate (monohydrate)	Permanganate	184.22	0.09211	0.3684
	Ceric Sulphate			
Potassium Permanganate	Ferrous Ammonium Sulphate	158.03	0.03161	0.1264
	Ferrous Sulphate			
Silver Nitrate	Iodine	169.89	0.16989	0.6796
Sodium Bromate	Thiosulphate	150.91	0.02515	0.1006
Sodium Iodate	Thiosulphate	197.92	0.03299	0.1320
Sodium Oxalate	Permanganate	133.99	0.0670	0.2680
	Ceric Sulphate			
Sodium Thiosulphate (pentahydrate)	Iodine	248.19	0.24819	0.9928
	Bromate			
	Iodate			
Thallous Carbonate	Iodate	468.78	0.1172	0.4688

PRECIPITATION

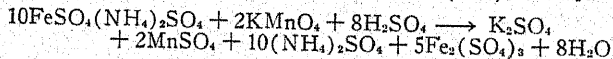
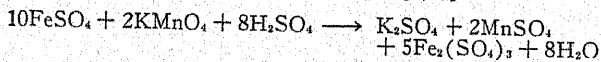
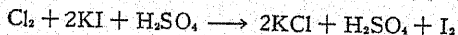
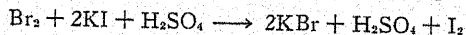
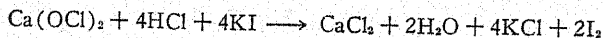
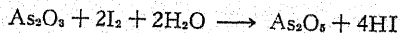
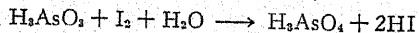
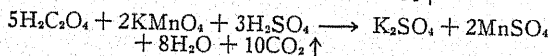
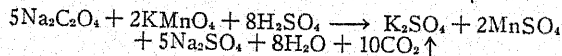
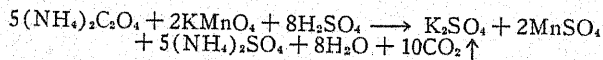
Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for N/10 Solutions
Ammonium Thiocyanate	Silver Nitrate	76.11	0.07611	0.3044
Potassium Thiocyanate	Silver Nitrate	97.17	0.09717	0.3887
Silver Nitrate	Thiocyanate	169.89	0.16989	0.6796
Sodium Chloride	Silver Nitrate	58.45	0.05845	0.2338
Zinc Oxide	Potassium Ferrocyanide	422.33	0.21117	0.8447

EQUATIONS INVOLVED IN STANDARDIZATION

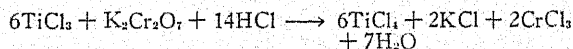
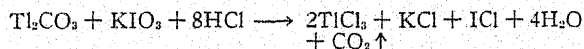
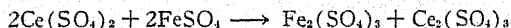
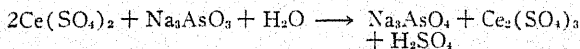
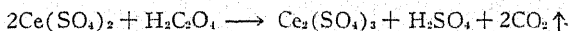
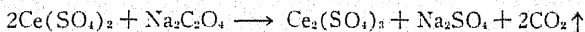
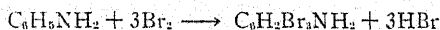
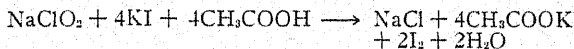
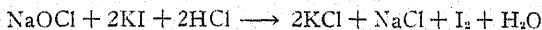
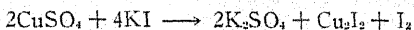
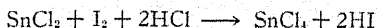
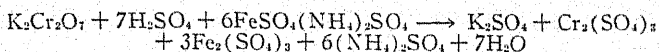
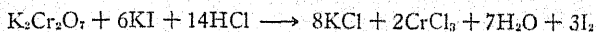
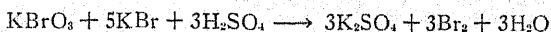
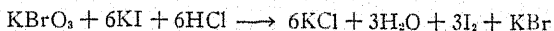
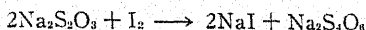
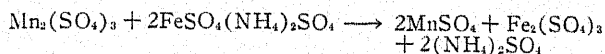
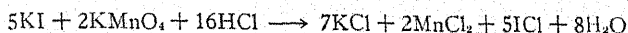
ACID-BASE



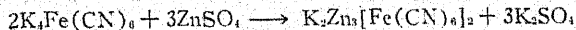
OXIDATION-REDUCTION



OXIDATION-REDUCTION



PRECIPITATION



LOGARITHMS OF VOLUMETRIC FACTORS BASED ON THE VALUE OF A NORMAL SOLUTION

ACID-BASE

Compound	Formula	Milli-Equiv- alent	Loga- rithm
Ammonium Hydroxide	NH_4OH	0.03505	$\bar{2}.54469$
Barium Hydroxide	$\text{Ba}(\text{OH})_2$	0.08569	$\bar{2}.93293$
Hydrochloric Acid	HCl	0.036465	$\bar{2}.56189$
Potassium Acid Phthalate	$\text{KHO}_2\text{C}_6\text{H}_4$	0.20406	$\bar{1}.30976$
Potassium Biiodate	$\text{KH}(\text{IO}_3)_2$	0.3899	$\bar{1}.59095$
Potassium Hydroxide	KOH	0.05610	$\bar{2}.74896$
Silver Chloride	AgCl	0.14334	$\bar{1}.15637$
Sodium Tetraborate	$\text{Na}_2\text{B}_4\text{O}_7$	0.10072	$\bar{1}.00312$
Sodium Tetraborate (Hydrated)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.19072	$\bar{1}.28040$
Sodium Carbonate	Na_2CO_3	0.0530	$\bar{2}.72428$
Sodium Hydroxide	NaOH	0.0400	$\bar{2}.60206$
Sulphuric Acid	H_2SO_4	0.04904	$\bar{2}.69055$

LOGARITHMS OF VOLUMETRIC FACTORS
BASED ON THE VALUE OF A
NORMAL SOLUTION

OXIDATION-REDUCTION

Compound	Formula	Milli-Equiv- alent	Loga- rithm
Arsenious Acid	As_2O_3	0.04946	$\bar{2}.69425$
Calcium Hypochlorite	$\text{Ca}(\text{OCI})_2$	0.06350	$\bar{2}.80277$
Ceric Sulphate	$\text{Ce}(\text{SO}_4)_2$	0.33225	$\bar{1}.52147$
Chloramine T	$\text{p-C}_6\text{H}_4\text{CH}_3\text{SO}_2\text{N} \begin{smallmatrix} \nearrow \text{Na} \\ \searrow \text{Cl} \end{smallmatrix}$	0.14075	$\bar{1}.14845$
Copper	Cu	0.06357	$\bar{2}.80325$
Copper Sulphate	CuSO_4	0.15963	$\bar{1}.20311$
Ferrous Ammonium Sul- phate (Mohr's Salt)	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	0.39190	$\bar{1}.59318$
Ferrous Sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.27801	$\bar{1}.44406$
Iodine	I	0.12692	$\bar{1}.10353$
Oxalic Acid	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	0.06303	$\bar{2}.79955$
Potassium Bromate	KBrO_3	0.02784	$\bar{2}.44467$
Potassium Dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$	0.04904	$\bar{2}.69055$
Potassium Iodate	KIO_3	0.03567	$\bar{2}.55230$
Potassium Permanganate	KMnO_4	0.03161	$\bar{2}.49982$
Sodium Hypochlorite	NaOCI	0.037227	$\bar{2}.57086$
Sodium Oxalate	$\text{Na}_2\text{C}_2\text{O}_4$	0.066995	$\bar{2}.82604$
Sodium Thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3$	0.15811	$\bar{1}.19896$
Sodium Thiosulphate (Hydrated)	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.24819	$\bar{1}.39478$
Titanium Chloride	TiCl_3	0.15427	$\bar{1}.18828$
Titanium Sulphate	$\text{Ti}_2(\text{SO}_4)_3$	0.38398	$\bar{1}.58431$

PRECIPITATION

Compound	Formula	Milli-Equivalent	Logarithm
Ammonium Thiocyanate	NH ₄ SCN	0.07611	2.88144
Potassium Ferrocyanide	K ₄ Fe(CN) ₆ · 3H ₂ O	0.21117	1.32463
Potassium Thiocyanate	KSCN	0.09717	2.98753
Silver Nitrate	AgNO ₃	0.16989	1.23017
Sodium Chloride	NaCl	0.05845	2.76678

ABSOLUTE DENSITY OF WATER *

This table gives the weight in grams of a cubic centimeter of water at temperatures from 0° to 30°C. Water attains its maximum density at 3.98°C. at which temperature the density is 0.999973 (C. G. S.)

Temp. °C.	Density	Temp. °C.	Density	Temp. °C.	Density	Temp. °C.	Density
0.0	0.999841	7.6	0.999872	15.2	0.999069	22.8	0.997585
0.2	9854	7.8	9861	15.4	9038	23.0	7538
0.4	8866	8.0	9849	15.6	9007	23.2	7490
0.6	9878	8.2	9837	15.8	8975	23.4	7442
0.8	9889	8.4	9824	16.0	8943	23.6	7394
1.0	9900	8.6	9810	16.2	8910	23.8	7345
1.2	9909	8.8	9796	16.4	8877	24.0	7296
1.4	9918	9.0	9781	16.6	8843	24.2	7246
1.6	9927	9.2	9766	16.8	8809	24.4	7196
1.8	9934	9.4	9751	17.0	8774	24.6	7146
2.0	9941	9.6	9734	17.2	8739	24.8	7095
2.2	9947	9.8	9717	17.4	8704	25.0	7044
2.4	9953	10.0	9700	17.6	8668	25.2	6992
2.6	9958	10.2	9682	17.8	8632	25.4	6941
2.8	9962	10.4	9664	18.0	8595	25.6	6888
3.0	9965	10.6	9645	18.2	8558	25.8	6836
3.2	9968	10.8	9625	18.4	8520	26.0	6783
3.4	9970	11.0	9605	18.6	8482	26.2	6729
3.6	9972	11.2	9585	18.8	8444	26.4	6676
3.8	9973	11.4	9564	19.0	8405	26.6	6621
4.0	9973	11.6	9542	19.2	8365	26.8	6567
4.2	9973	11.8	9520	19.4	8325	27.0	6512
4.4	9972	12.0	9498	19.6	8285	27.2	6457
4.6	9970	12.2	9475	19.8	8244	27.4	6401
4.8	9968	12.4	9451	20.0	8203	27.6	6345
5.0	9965	12.6	9427	20.2	8152	27.8	6289
5.2	9961	12.8	9402	20.4	8120	28.0	6232
5.4	9957	13.0	9377	20.6	8078	28.2	6175
5.6	9952	13.2	9352	20.8	8035	28.4	6118
5.8	9947	13.4	9326	21.0	7992	28.6	6060
6.0	9941	13.6	9299	21.2	7948	28.8	6002
6.2	9935	13.8	9272	21.4	7904	29.0	5944
6.4	9927	14.0	9244	21.6	7860	29.2	5885
6.6	9920	14.2	9216	21.8	7815	29.4	5826
6.8	9911	14.4	9188	22.0	7770	29.6	5766
7.0	9902	14.6	9159	22.2	7724	29.8	5706
7.2	8893	14.8	9129	22.4	7678	30.0	5646
7.4	8883	15.0	9099	22.6	7632		

* Reprinted, by permission, from Lange's Handbook of Chemistry, published by Handbook Publishers, Inc., Sandusky, Ohio.

HYDRATION TEMPERATURES, MELTING POINTS, AND BOILING POINTS FOR CALIBRATION OF THERMOMETERS

Compound	Formula	Hydration Temperature
Sodium Chromate	$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$	19.71° C
Sodium Sulphate	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	32.383
Sodium Carbonate	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$	35.3
Sodium Thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	48.0
Sodium Bromide	$\text{NaBr} \cdot 2\text{H}_2\text{O}$	50.8
Manganese Chloride	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	57.8
Trisodium Phosphate	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	73.4
Barium Hydroxide	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	78.0

		Melting Points
Naphthalene	C_{10}H_8	80.8° C
Phenanthrene	$(\text{C}_6\text{H}_4\text{CH})_2$	101.0
Benzoic Acid	$\text{C}_6\text{H}_5\text{COOH}$	122.45
Salicylic Acid	$\text{HO} \cdot \text{C}_6\text{H}_4\text{COOH}$	159.8
Anisic Acid	$\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$	184.2
Anthracene	$(\text{C}_6\text{H}_4\text{CH})_2$	216.1
Carbazole	$\text{C}_6\text{H}_4\text{NH} \cdot \text{C}_6\text{H}_4$	247.0
Anthraquinone	$(\text{C}_6\text{H}_4)_2(\text{CO})_2$	285.0

		Boiling Points @ 760 mm
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	110.5° C
Monochlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	132.1
Monobromobenzene	$\text{C}_6\text{H}_5\text{Br}$	156.2

REFERENCES

- J. Phys. Chem.* 6, 85 (1902).
P. W. Richards and A. H. Fiske, *J. Am. Chem. Soc.* 36,
485 (1914).
H. C. Dickinson and E. F. Mueller, *J. Am. Chem. Soc.*
29, 1381 (1907).

LOGARITHMS OF NUMBERS

100 — 150

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts			
100		00	000	043	087	130	173	217	260	303	346	389	44	43	42
101			432	475	518	561	604	647	689	732	775	817	1	4.4	4.3
102			850	903	945	988	*030	*072	*115	*157	*199	*242	2	8.8	8.6
103	01		284	326	368	410	452	*494	536	578	620	662	3	13.2	12.9
104			703	745	787	828	870	912	953	995	*036	*078	4	17.6	17.2
105	02	119	160	202	243	284	325	366	407	449	490		5	22.0	21.5
106			531	572	612	653	694	735	776	816	857	898	6	26.4	25.8
107			938	979	*019	*060	*100	*141	*181	*222	*262	*302	7	30.8	30.1
108	03		342	383	423	463	503	543	583	623	663	703	8	35.2	34.4
109			743	782	822	862	902	941	981	*021	*060	*100	9	39.6	38.7
110	04	139	179	218	258	297	336	376	415	454	493		10	44	40
111			532	571	610	650	689	727	765	805	844	883	11	4.1	4.0
112			922	961	999	*038	*077	*115	*154	*192	*231	*269	12	8.2	8.0
113	05	308	346	385	423	461	500	538	576	614	652		13	12.3	12.0
114			690	729	767	805	843	881	918	956	994	*032	14	16.4	16.0
115	06	070	108	145	183	221	258	296	333	371	408		15	20.5	20.0
116			446	483	521	558	595	633	670	707	744	781	16	24.6	24.0
117			819	856	893	930	967	*004	*041	*078	*115	*151	17	28.7	28.0
118	07	189	225	262	298	335	372	408	445	482	518		18	32.8	32.0
119			555	591	628	664	700	737	773	809	846	882	19	36.9	36.0
120			918	954	990	*027	*063	*099	*135	*171	*207	*243	20	38	37
121	08	279	314	350	386	422	458	493	529	565	600		21	3.8	3.7
122			636	672	707	743	778	814	849	884	920	955	22	7.6	7.4
123			991	*026	*061	*096	*132	*167	*202	*237	*272	*307	23	11.4	11.1
124	09	342	377	412	447	482	517	552	587	621	656		24	15.2	14.8
125			691	726	760	795	830	864	899	934	968	*003	25	19.0	18.5
126	10	037	072	106	140	175	209	243	278	312	346		26	22.8	22.2
127			380	415	449	483	517	551	585	619	653	687	27	26.6	25.9
128			721	755	789	823	857	890	924	958	992	*025	28	30.4	29.6
129	11	059	093	126	160	193	227	261	294	327	361		29	34.2	33.3
130			394	428	461	494	528	561	594	628	661	694	30	35	34
131			727	760	793	826	860	893	926	959	992	*024	31	3.5	3.4
132	12	057	090	123	156	189	222	254	287	320	352		32	7.0	6.8
133			385	418	450	483	516	548	581	613	646	678	33	10.5	10.2
134			710	743	775	808	840	872	905	937	969	*001	34	14.0	13.6
135	13	033	066	098	130	162	194	226	258	290	322		35	17.5	17.0
136			354	386	418	450	481	513	545	577	609	640	36	21.0	20.4
137			672	704	735	767	799	830	862	893	925	956	37	24.5	23.8
138			988	*019	*051	*082	*114	*145	*176	*208	*239	*270	38	28.0	27.2
139	14	301	333	364	395	425	457	489	520	551	582		39	31.5	30.6
140			613	644	675	706	737	768	799	829	860	891	40	32	31
141			922	953	983	*014	*045	*076	*106	*137	*168	*198	41	3.2	3.1
142	15	229	259	290	320	351	381	412	442	473	503		42	6.4	6.2
143			534	564	594	625	655	685	715	746	776	806	43	9.6	9.3
144			836	866	897	927	957	987	*017	*047	*077	*107	44	12.8	12.4
145	16	137	167	197	227	256	286	316	346	376	406		45	16.0	15.5
146			435	465	495	524	554	584	613	643	673	702	46	19.2	18.6
147			732	761	791	820	850	879	909	938	967	997	47	22.4	21.7
148	17	026	056	085	114	143	173	202	231	260	289		48	25.6	24.8
149			319	348	377	406	435	464	493	522	551	580	49	28.8	27.9
150			609	638	667	696	725	754	782	811	840	869	50	32.0	31.0
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts			

.00000 — .17869

LOGARITHMS OF NUMBERS

150 — 200

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
150	17	609	638	667	696	725	754	782	811	840	869	29 28
151		898	926	955	984	*013	*041	*070	*099	*127	*156	1 2.9 2.8
152	18	134	213	241	270	298	327	355	384	412	441	2 5.8 5.6
153		469	498	526	554	583	611	639	667	696	724	3 8.7 8.4
154		752	780	808	837	865	893	921	949	977	*005	4 11.6 11.2
155	19	033	061	089	117	145	173	201	229	257	285	5 14.5 14.0
156		312	340	368	396	424	451	479	507	535	562	6 17.4 16.8
157		590	618	645	673	700	728	755	783	811	838	7 20.3 19.6
158		866	893	921	948	976	*003	*030	*058	*085	*112	8 23.2 22.4
159	20	140	167	194	222	249	276	303	330	358	385	9 26.1 25.2
160		412	439	466	493	520	548	575	602	629	656	1 27 26
161		583	710	737	763	790	817	844	871	898	925	2 2.7 2.6
162		952	978	*005	*032	*059	*085	*112	*139	*165	*192	3 5.4 5.2
163	21	219	245	272	299	325	352	378	405	431	458	4 8.1 7.8
164		484	511	537	564	590	617	643	669	696	722	5 10.8 10.4
165		748	775	801	827	854	880	906	932	958	985	6 13.5 13.0
166	22	011	037	063	089	115	141	167	194	220	246	7 16.2 15.6
167		272	298	324	350	376	401	427	453	479	505	8 18.9 18.2
168		531	557	583	608	634	660	686	712	737	763	9 21.6 20.8
169		789	814	840	866	891	917	943	968	994	*019	1 24.3 23.4
170	23	045	070	096	121	147	172	198	223	249	274	25
171		300	325	350	376	401	426	452	477	502	528	1 2.3
172		553	578	603	629	654	679	704	729	754	779	2 5.0
173		805	830	855	880	905	930	955	980	*005	*030	3 7.5
174	24	055	080	105	130	155	180	204	228	254	279	4 10.0
175		304	329	353	378	403	428	452	477	502	527	5 12.5
176		551	576	601	625	650	674	699	724	748	773	6 15.0
177		797	822	846	871	895	920	944	969	993	*018	7 17.5
178	25	042	066	091	115	139	164	188	212	237	261	8 20.0
179		285	310	334	358	382	406	431	455	479	503	9 22.5
180		527	551	575	600	624	648	672	696	720	744	1 24 23
181		768	792	816	840	864	888	912	935	959	983	2 2.7 2.3
182	26	007	031	055	079	102	126	150	174	198	221	3 4.8 4.6
183		245	269	293	316	340	364	387	411	435	458	4 7.2 6.9
184		482	505	529	553	576	600	623	647	670	694	5 9.6 9.2
185		717	741	764	788	811	834	858	881	905	928	6 12.0 11.5
186		951	975	998	*021	*045	*068	*091	*114	*138	*161	7 14.4 13.8
187	27	184	207	231	254	277	300	323	346	370	393	8 16.8 16.1
188		416	439	462	485	508	531	554	577	600	623	9 19.2 18.4
189		646	669	692	715	738	761	784	807	830	852	1 21.6 20.7
190		875	898	921	944	967	989	*012	*035	*058	*081	2 22 21
191	28	103	126	149	171	194	217	240	262	285	307	3 2.3 2.1
192		330	353	375	398	421	443	466	488	511	533	4 4.4 4.2
193		556	578	601	623	646	668	691	713	735	758	5 6.6 6.3
194		780	803	825	847	870	892	914	937	959	981	6 8.8 8.4
195	29	003	026	048	070	092	115	137	159	181	203	7 11.0 10.5
196		226	248	270	292	314	336	358	380	403	425	8 13.2 12.6
197		447	469	491	513	535	557	579	601	623	645	9 15.4 14.7
198		667	688	710	732	754	776	798	820	842	863	1 17.6 16.8
199		885	907	929	951	973	994	*016	*038	*060	*081	2 19.8 18.9
200	30	103	125	146	168	190	211	233	255	276	298	
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

.17 609 — .30 298

LOGARITHMS OF NUMBERS

200 — 250

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
200		30	103	125	146	168	190	211	233	255	276	298
201		320	341	363	384	405	428	449	471	492	514	536
202		535	557	578	600	621	643	664	685	707	728	749
203		750	771	792	814	835	856	878	899	920	942	963
204		963	984	*006	*027	*048	*069	*091	*112	*133	*154	
205	31	175	197	218	239	260	281	302	323	345	366	
206		387	408	429	450	471	492	513	534	555	576	
207		597	618	639	660	681	702	723	744	765	785	
208		806	827	848	869	890	911	931	952	973	994	
209	32	015	035	056	077	098	118	139	160	181	201	
210		222	243	263	284	305	325	346	366	387	408	
211		428	449	469	490	510	531	552	572	593	613	
212		634	654	675	695	715	736	756	777	797	818	
213		838	858	879	899	919	940	960	980	*001	*021	
214	33	041	062	082	102	122	143	163	183	203	224	
215		244	264	284	304	325	345	365	385	405	425	
216		445	465	485	505	525	546	566	586	606	626	
217		646	666	686	706	726	746	766	786	806	826	
218		846	866	885	905	925	945	965	985	*005	*025	
219	34	044	064	084	104	124	143	163	183	203	223	
220		242	262	282	301	321	341	361	380	400	420	
221		439	459	479	498	518	537	557	577	596	616	
222		635	655	674	694	713	733	753	772	792	811	
223		830	850	869	889	908	928	947	967	986	*005	
224	35	025	044	064	083	102	122	141	160	180	199	
225		218	238	257	276	295	315	334	353	372	392	
226		411	430	449	468	488	507	526	545	564	583	
227		603	622	641	660	679	698	717	736	755	774	
228		793	813	832	851	870	889	908	927	946	965	
229		984	*003	*021	*040	*059	*078	*097	*116	*135	*154	
230	36	173	192	211	229	248	267	286	305	324	342	
231		361	380	399	418	436	455	474	493	511	530	
232		549	568	586	605	624	642	661	680	698	717	
233		736	754	773	791	810	829	847	866	884	903	
234		922	940	959	977	996	*014	*033	*051	*070	*088	
235	37	107	125	144	162	181	199	218	236	254	273	
236		221	310	328	346	365	383	401	420	438	457	
237		475	493	511	530	548	566	585	603	621	639	
238		658	676	694	712	731	749	767	785	803	822	
239		840	858	876	894	912	931	949	967	985	*003	
240	38	021	039	057	075	093	112	130	148	166	184	
241		202	220	238	256	274	292	310	328	346	364	
242		382	399	417	435	453	471	489	507	525	543	
243		561	578	596	614	632	650	668	686	703	721	
244		739	757	775	792	810	828	846	863	881	899	
245		917	934	952	970	987	*005	*023	*041	*058	*076	
246	39	094	111	129	146	164	182	199	217	235	252	
247		270	287	305	322	340	358	375	393	410	428	
248		445	463	480	498	515	533	550	568	585	602	
249		620	637	655	672	690	707	724	742	759	777	
250		794	811	829	846	863	881	898	915	933	950	
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

.30 103 — .59 950

LOGARITHMS OF NUMBERS

250 — 300

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
250	39	794	811	829	846	863	881	898	915	933	950	18
251		967	985	*002	*019	*037	*054	*071	*088	*106	*123	1 1.8
252	40	140	157	175	192	209	226	243	261	278	295	2 3.6
253		312	329	346	364	381	398	415	432	449	466	3 5.4
254		483	500	518	535	552	569	586	603	620	637	4 7.2
255		654	671	688	705	722	739	756	773	790	807	5 9.0
256		824	841	858	875	892	909	926	943	960	976	6 10.8
257		993	*010	*027	*044	*061	*078	*095	*111	*128	*145	7 12.6
258	41	162	179	196	212	229	246	263	280	296	313	8 14.4
259		330	347	363	380	397	414	430	447	464	481	9 16.2
260		497	514	531	547	564	581	597	614	631	647	17
261		664	681	697	714	731	747	764	780	797	814	1 1.7
262		830	847	863	880	896	913	929	946	963	979	2 3.4
263		996	*012	*029	*045	*062	*078	*095	*111	*127	*144	3 5.1
264	42	160	177	193	210	226	243	259	275	292	308	4 6.8
265		325	341	357	374	390	406	423	439	455	472	5 8.5
266		488	504	521	537	553	570	586	602	619	635	6 10.2
267		651	667	684	700	716	732	749	765	781	797	7 11.9
268		813	830	846	862	878	894	911	927	943	959	8 13.6
269		975	991	*008	*024	*040	*056	*072	*088	*104	*120	9 15.3
270	43	136	152	169	185	201	217	233	249	265	281	16
271		297	313	329	345	361	377	393	409	425	441	1 1.6
272		457	473	489	505	521	537	553	569	584	600	2 3.2
273		616	632	648	664	680	696	712	727	743	759	3 4.8
274		775	791	807	823	838	854	870	886	902	917	4 6.4
275		933	949	965	981	996	*012	*028	*044	*059	*075	5 8.0
276	44	091	107	122	138	154	170	185	201	217	232	6 9.6
277		248	264	279	295	311	326	342	358	373	389	7 11.2
278		404	420	436	451	467	483	498	514	529	545	8 12.8
279		560	576	592	607	623	638	654	669	685	700	9 14.4
280		716	731	747	762	778	793	809	824	840	855	15
281		871	886	902	917	932	948	963	979	994	*010	1 1.5
282	45	025	040	056	071	086	102	117	133	148	163	2 3.0
283		179	194	209	225	240	255	271	286	301	317	3 4.5
284		332	347	362	378	393	408	423	439	454	469	4 6.0
285		484	500	515	530	545	561	576	591	606	621	5 7.5
286		637	652	667	682	697	712	728	743	758	773	6 9.0
287		788	803	818	834	849	864	879	894	909	924	7 10.5
288		939	954	969	984	*000	*015	*030	*045	*060	*075	8 12.0
289	46	090	105	120	135	150	165	180	195	210	225	9 13.5
290		240	255	270	285	300	315	330	345	359	374	14
291		389	404	419	434	449	464	479	494	509	523	1 1.4
292		538	553	568	583	598	613	627	642	657	672	2 2.8
293		687	702	716	731	746	761	776	790	805	820	3 4.2
294		835	850	864	879	894	909	923	938	953	967	4 5.6
295		982	997	*012	*026	*041	*056	*070	*085	*100	*114	5 7.0
296	47	129	144	159	173	188	202	217	232	246	261	6 8.4
297		275	290	305	319	334	349	363	378	392	407	7 9.8
298		422	436	451	465	480	494	509	524	538	553	8 11.2
299		567	582	596	611	625	640	654	669	683	698	9 12.6
300		712	727	741	756	770	784	799	813	828	842	log $\epsilon = 0.43429$
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

.39 794 — .47 842

LOGARITHMS OF NUMBERS

300 — 350

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
300	47	712	727	741	756	770	784	799	813	828	842	
301		857	871	885	900	914	929	943	958	972	986	
302	48	001	015	029	044	058	073	087	101	116	130	
303		144	159	173	187	202	216	230	244	259	273	
304		287	302	316	330	344	359	373	387	401	416	
305		430	444	458	473	487	501	515	530	544	558	
306		572	586	601	615	629	643	657	671	686	700	
307		714	728	742	756	770	785	799	813	827	841	
308		855	869	883	897	911	926	940	954	968	982	
309		996	*010	*024	*038	*052	*066	*080	*094	*108	*122	
310	49	136	150	164	178	192	206	220	234	248	262	
311		276	290	304	318	332	346	360	374	388	402	
312		415	429	443	457	471	485	499	513	527	541	
313		584	598	612	626	640	654	668	682	696	710	
314		693	707	721	734	748	762	776	790	803	817	
315		831	845	859	872	886	900	914	927	941	955	
316		969	982	996	*010	*024	*037	*051	*065	*079	*092	
317	50	106	120	133	147	161	174	188	202	215	229	
318		243	256	270	284	297	311	325	338	352	365	
319		379	393	406	420	433	447	461	474	488	501	
320		515	529	542	556	569	583	596	610	623	637	
321		651	664	678	691	705	718	732	745	759	772	
322		786	799	813	826	840	853	866	880	893	907	
323		920	934	947	961	974	987	*001	*014	*028	*041	
324	51	055	068	081	095	108	121	135	148	162	175	
325		188	202	215	228	242	255	268	282	295	308	
326		322	335	348	362	375	388	402	415	428	441	
327		455	468	481	495	508	521	534	548	561	574	
328		587	601	614	627	640	654	667	680	693	706	
329		720	733	746	759	772	786	799	812	825	838	
330		851	865	878	891	904	917	930	943	957	970	
331		983	996	*009	*022	*035	*048	*061	*075	*088	*101	
332	52	114	127	140	153	166	179	192	205	218	231	
333		244	257	270	284	297	310	323	336	349	362	
334		375	388	401	414	427	440	453	466	479	492	
335		504	517	530	543	556	569	582	595	608	621	
336		634	647	660	673	686	699	711	724	737	750	
337		763	776	789	802	815	827	840	853	866	879	
338		892	905	917	930	943	956	969	982	994	*007	
339	53	020	033	046	058	071	084	097	110	122	135	
340		148	161	173	186	199	212	224	237	250	263	
341		275	288	301	314	326	339	352	364	377	390	
342		403	415	428	441	453	466	479	491	504	517	
343		529	542	555	567	580	593	605	618	631	643	
344		656	668	681	694	706	719	732	744	757	769	
345		782	794	807	820	832	845	857	870	882	895	
346		908	920	933	945	958	970	983	995	*008	*020	
347	54	033	045	058	070	083	095	108	120	133	145	
348		158	170	183	195	208	220	233	245	258	270	
349		283	295	307	320	332	345	357	370	382	394	
350		407	419	432	444	456	469	481	494	506	518	
N.	L.	0	1	2	3	4	5	6	7	8	9	log x = 0.49715
												Proportional parts

47 712 --- .54 518

LOGARITHMS OF NUMBERS

350 — 400

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
350	54	407	419	432	444	456	469	481	494	506	518	
351		531	543	555	568	580	593	605	617	630	642	
352		654	667	679	691	704	716	728	741	753	765	
353		777	790	802	814	827	839	851	864	876	888	
354		900	913	925	937	949	962	974	986	998	*011	13
355	55	023	035	047	060	072	084	096	108	121	133	1 1.3
356		145	157	169	182	194	206	218	230	242	255	2 2.6
357		267	279	291	303	315	328	340	352	364	376	3 3.9
358		388	400	413	425	437	449	461	473	485	497	4 5.2
359		509	522	534	546	558	570	582	594	606	618	5 6.5
360		630	642	654	666	678	691	703	715	727	739	6 7.8
361		751	763	775	787	799	811	823	835	847	859	7 9.1
362		871	883	895	907	919	931	943	955	967	979	8 10.4
363		991	*003	*015	*027	*038	*050	*062	*074	*086	*098	9 11.7
364	56	110	122	134	146	158	170	182	194	205	217	
365		229	241	253	265	277	289	301	312	324	336	12
366		348	360	372	384	396	407	419	431	443	455	1 1.2
367		467	478	490	502	514	526	538	549	561	573	2 2.4
368		585	597	608	620	632	644	656	667	679	691	3 3.6
369		703	714	726	738	750	761	773	785	797	808	4 4.8
370		820	832	844	855	867	879	891	902	914	926	5 6.0
371		937	949	961	972	984	996	*008	*019	*031	*043	6 7.2
372	57	054	066	078	089	101	113	124	136	148	159	7 8.4
373		171	183	194	206	217	229	241	252	264	276	8 9.6
374		287	299	310	322	334	345	357	368	380	392	9 10.8
375		403	415	426	438	449	461	473	484	496	507	
376		519	530	542	553	565	576	588	600	611	623	11
377		634	646	657	669	680	692	703	715	726	738	1 1.1
378		749	761	772	784	795	807	818	830	841	852	2 2.2
379		864	875	887	898	910	921	933	944	955	967	3 3.3
380		978	990	*001	*013	*024	*035	*047	*058	*070	*081	4 4.4
381	58	092	104	115	127	138	149	161	172	184	195	5 5.5
382		206	218	229	240	252	263	274	286	297	309	6 6.6
383		320	331	343	354	365	377	388	399	410	422	7 7.7
384		433	444	456	467	478	490	501	512	524	535	8 8.8
385		546	557	569	580	591	602	614	625	636	647	9 9.9
386		659	670	681	692	704	715	726	737	749	760	
387		771	782	794	805	816	827	838	850	861	872	
388		883	894	906	917	928	939	950	961	973	984	
389		995	*006	*017	*028	*040	*051	*062	*073	*084	*095	10
390	59	106	118	129	140	151	162	173	184	195	207	1 1.0
391		218	229	240	251	262	273	284	295	306	318	2 2.0
392		329	340	351	362	373	384	395	406	417	428	3 3.0
393		439	450	461	472	483	494	506	517	528	539	4 4.0
394		550	561	572	583	594	605	616	627	638	649	5 5.0
395		660	671	682	693	704	715	726	737	748	759	6 6.0
396		770	780	791	802	813	824	835	846	857	868	7 7.0
397		879	890	901	912	923	934	945	956	966	977	8 8.0
398		988	999	*010	*021	*032	*043	*054	*065	*076	*086	9 9.0
399	60	097	108	119	130	141	152	163	173	184	195	
400		206	217	228	239	249	260	271	282	293	304	
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

.54 407 — .60 304

LOGARITHMS OF NUMBERS

400 — 450

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
400	60	206	217	228	239	249	260	271	282	293	304	1
401	314	325	336	347	358	369	379	390	401	412	423	2
402	433	443	454	465	476	487	498	509	520	531	542	3
403	551	561	572	583	594	605	616	627	637	648	659	4
404	669	680	690	701	712	723	734	745	756	767	778	5
405	789	799	810	821	832	843	854	865	876	887	898	6
406	909	920	931	942	953	964	975	986	997	1008	1019	7
407	1030	1041	1052	1063	1074	1085	1096	1107	1118	1129	1140	8
408	1151	1162	1173	1184	1195	1206	1217	1228	1239	1250	1261	9
409	1272	1283	1294	1305	1316	1327	1338	1349	1360	1371	1382	10
410	1393	1404	1415	1426	1437	1448	1459	1470	1481	1492	1503	1
411	1514	1525	1536	1547	1558	1569	1580	1591	1602	1613	1624	2
412	1635	1646	1657	1668	1679	1690	1701	1712	1723	1734	1745	3
413	1756	1767	1778	1789	1800	1811	1822	1833	1844	1855	1866	4
414	1877	1888	1899	1910	1921	1932	1943	1954	1965	1976	1987	5
415	1998	2009	2020	2031	2042	2053	2064	2075	2086	2097	2108	6
416	2119	2130	2141	2152	2163	2174	2185	2196	2207	2218	2229	7
417	2240	2251	2262	2273	2284	2295	2306	2317	2328	2339	2350	8
418	2361	2372	2383	2394	2405	2416	2427	2438	2449	2460	2471	9
419	2482	2493	2504	2515	2526	2537	2548	2559	2570	2581	2592	10
420	2603	2614	2625	2636	2647	2658	2669	2680	2691	2702	2713	1
421	2724	2735	2746	2757	2768	2779	2790	2801	2812	2823	2834	2
422	2845	2856	2867	2878	2889	2900	2911	2922	2933	2944	2955	3
423	2966	2977	2988	2999	3010	3021	3032	3043	3054	3065	3076	4
424	3087	3098	3109	3120	3131	3142	3153	3164	3175	3186	3197	5
425	3208	3219	3230	3241	3252	3263	3274	3285	3296	3307	3318	6
426	3329	3340	3351	3362	3373	3384	3395	3406	3417	3428	3439	7
427	3450	3461	3472	3483	3494	3505	3516	3527	3538	3549	3560	8
428	3571	3582	3593	3604	3615	3626	3637	3648	3659	3670	3681	9
429	3692	3703	3714	3725	3736	3747	3758	3769	3780	3791	3802	10
430	3813	3824	3835	3846	3857	3868	3879	3890	3901	3912	3923	1
431	3934	3945	3956	3967	3978	3989	4000	4011	4022	4033	4044	2
432	4055	4066	4077	4088	4099	4110	4121	4132	4143	4154	4165	3
433	4176	4187	4198	4209	4220	4231	4242	4253	4264	4275	4286	4
434	4297	4308	4319	4330	4341	4352	4363	4374	4385	4396	4407	5
435	4418	4429	4440	4451	4462	4473	4484	4495	4506	4517	4528	6
436	4539	4550	4561	4572	4583	4594	4605	4616	4627	4638	4649	7
437	4660	4671	4682	4693	4704	4715	4726	4737	4748	4759	4770	8
438	4781	4792	4803	4814	4825	4836	4847	4858	4869	4880	4891	9
439	4902	4913	4924	4935	4946	4957	4968	4979	4990	5001	5012	10
440	5023	5034	5045	5056	5067	5078	5089	5100	5111	5122	5133	1
441	5144	5155	5166	5177	5188	5199	5210	5221	5232	5243	5254	2
442	5265	5276	5287	5298	5309	5320	5331	5342	5353	5364	5375	3
443	5386	5397	5408	5419	5430	5441	5452	5463	5474	5485	5496	4
444	5507	5518	5529	5540	5551	5562	5573	5584	5595	5606	5617	5
445	5628	5639	5650	5661	5672	5683	5694	5705	5716	5727	5738	6
446	5749	5760	5771	5782	5793	5804	5815	5826	5837	5848	5859	7
447	5870	5881	5892	5903	5914	5925	5936	5947	5958	5969	5980	8
448	5991	6002	6013	6024	6035	6046	6057	6068	6079	6090	6101	9
449	6112	6123	6134	6145	6156	6167	6178	6189	6200	6211	6222	10
450	6233	6244	6255	6266	6277	6288	6299	6310	6321	6332	6343	1
451	6354	6365	6376	6387	6398	6409	6420	6431	6442	6453	6464	2
452	6475	6486	6497	6508	6519	6530	6541	6552	6563	6574	6585	3
453	6596	6607	6618	6629	6640	6651	6662	6673	6684	6695	6706	4
454	6717	6728	6739	6750	6761	6772	6783	6794	6805	6816	6827	5
455	6838	6849	6860	6871	6882	6893	6904	6915	6926	6937	6948	6
456	6959	6970	6981	6992	7003	7014	7025	7036	7047	7058	7069	7
457	7080	7091	7102	7113	7124	7135	7146	7157	7168	7179	7190	8
458	7201	7212	7223	7234	7245	7256	7267	7278	7289	7300	7311	9
459	7322	7333	7344	7355	7366	7377	7388	7399	7410	7421	7432	10
460	7443	7454	7465	7476	7487	7498	7509	7520	7531	7542	7553	1
461	7564	7575	7586	7597	7608	7619	7630	7641	7652	7663	7674	2
462	7685	7696	7707	7718	7729	7740	7751	7762	7773	7784	7795	3
463	7806	7817	7828	7839	7850	7861	7872	7883	7894	7905	7916	4
464	7927	7938	7949	7960	7971	7982	7993	8004	8015	8026	8037	5
465	8048	8059	8070	8081	8092	8103	8114	8125	8136	8147	8158	6
466	8169	8180	8191	8202	8213	8224	8235	8246	8257	8268	8279	7
467	8290	8301	8312	8323	8334	8345	8356	8367	8378	8389	8400	8
468	8411	8422	8433	8444	8455	8466	8477	8488	8499	8510	8521	9
469	8532	8543	8554	8565	8576	8587	8598	8609	8620	8631	8642	10
470	8653	8664	8675	8686	8697	8708	8719	8730	8741	8752	8763	1
471	8774	8785	8796	8807	8818	8829	8840	8851	8862	8873	8884	2
472	8895	8906	8917	8928	8939	8950	8961	8972	8983	8994	9005	3
473	9016	9027	9038	9049	9060	9071	9082	9093	9104	9115	9126	4
474	9137	9148	9159	9170	9181	9192	9203	9214	9225	9236	9247	5
475	9258	9269	9280	9291	9302	9313	9324	9335	9346	9357	9368	6
476	9379	9390	9401	9412	9423	9434	9445	9456	9467	9478	9489	7
477	9500	9511	9522	9533	9544	9555	9566	9577	9588	9599	9610	8
478	9621	9632	9643	9654	9665	9676	9687	9698	9709	9720	9731	9
479	9742	9753	9764	9775	9786	9797	9808	9819	9830	9841	9852	10
480	9863	9874	9885	9896	9907	9918	9929	9940	9951	9962	9973	1
481	9984	9995	10006	10017	10028	10039	10050	10061	10072	10083	10094	2
482	10105	10116	10127	10138	10149	10160	10171	10182	10193	10204	10215	3
483	10226	10237	10248	10259	10270	10281	10292	10303	10314	10325	10336	4
484	10347	10358	10369	10380	10391	10402	10413	10424	10435	10446	10457	5
485	10468	10479	10490	10501	10512	10523	10534	10545	10556	10567	10578	6
486	10589	10600	10611	10622	10633	10644	10655	10666	10677	10688	10699	7
487	10710	10721	10732	10743	10754	10765	10776	10787	10798	10809	10820	8
488	10831	10842	10853	10864	10875	10886	10897	10908	10919	10930	10941	9
489	10952	10963	10974	10985	10996	11007	11018	11029	11040	11051	11062	10
490	11073	11084	11095	11106	11117	11128	11139	11150	11161	11172	11183	1
491	11194	11205	11216	11227	11238	11249	11260	11271	11282	11293	11304	2
492	11315	11326	11337	11348	11359	11370	11381	11392	11403	11414	11425	3
493	11436	11447	11458	11469	11480	11491	11502	11513	11524	11535	11546	4
494	11557	11568	11579	11590	11601	11612	11623	11634	11645	11656	11667	5
495	11678	11689	11700	11711	11722	11733	11744	11755	11766	11777	11788	6
496	11799	11810	11821	11832	11843	11854	11865	11876	11887	11898	11909	7
497	11920	11931	11942	11953	11964	11975	11986	11997	12008	12019	12030	8
498	12041	12052	12063	12074	12085	12096	12107	12118	12129	12140	12151	9
499	12162	12173	12184	12195	12206	12217	12228	12239	12250	12261	12272	10

LOGARITHMS OF NUMBERS

450 — 500

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
450	65	371	331	291	250	209	168	127	86	45	408	10
451	66	372	332	292	251	210	169	128	87	46	409	1.0
452	67	373	333	293	252	211	170	129	88	47	410	2
453	68	374	334	294	253	212	171	130	89	48	411	3
454	69	375	335	295	254	213	172	131	90	49	412	4
455	70	376	336	296	255	214	173	132	91	50	413	5
456	71	377	337	297	256	215	174	133	92	51	414	6
457	72	378	338	298	257	216	175	134	93	52	415	7
458	73	379	339	299	258	217	176	135	94	53	416	8
459	74	380	340	300	259	218	177	136	95	54	417	9
460	75	381	341	301	260	219	178	137	96	55	418	10
461	76	382	342	302	261	220	179	138	97	56	419	1.0
462	77	383	343	303	262	221	180	139	98	57	420	2
463	78	384	344	304	263	222	181	140	99	58	421	3
464	79	385	345	305	264	223	182	141	100	59	422	4
465	80	386	346	306	265	224	183	142	101	60	423	5
466	81	387	347	307	266	225	184	143	102	61	424	6
467	82	388	348	308	267	226	185	144	103	62	425	7
468	83	389	349	309	268	227	186	145	104	63	426	8
469	84	390	350	310	269	228	187	146	105	64	427	9
470	85	391	351	311	270	229	188	147	106	65	428	10
471	86	392	352	312	271	230	189	148	107	66	429	1.0
472	87	393	353	313	272	231	190	149	108	67	430	2
473	88	394	354	314	273	232	191	150	109	68	431	3
474	89	395	355	315	274	233	192	151	110	69	432	4
475	90	396	356	316	275	234	193	152	111	70	433	5
476	91	397	357	317	276	235	194	153	112	71	434	6
477	92	398	358	318	277	236	195	154	113	72	435	7
478	93	399	359	319	278	237	196	155	114	73	436	8
479	94	400	360	320	279	238	197	156	115	74	437	9
480	95	401	361	321	280	239	198	157	116	75	438	10
481	96	402	362	322	281	240	199	158	117	76	439	1.0
482	97	403	363	323	282	241	200	159	118	77	440	2
483	98	404	364	324	283	242	201	160	119	78	441	3
484	99	405	365	325	284	243	202	161	120	79	442	4
485	100	406	366	326	285	244	203	162	121	80	443	5
486	101	407	367	327	286	245	204	163	122	81	444	6
487	102	408	368	328	287	246	205	164	123	82	445	7
488	103	409	369	329	288	247	206	165	124	83	446	8
489	104	410	370	330	289	248	207	166	125	84	447	9
490	105	411	371	331	290	249	208	167	126	85	448	10
491	106	412	372	332	291	250	209	168	127	86	449	1.0
492	107	413	373	333	292	251	210	169	128	87	450	2
493	108	414	374	334	293	252	211	170	129	88	451	3
494	109	415	375	335	294	253	212	171	130	89	452	4
495	110	416	376	336	295	254	213	172	131	90	453	5
496	111	417	377	337	296	255	214	173	132	91	454	6
497	112	418	378	338	297	256	215	174	133	92	455	7
498	113	419	379	339	298	257	216	175	134	93	456	8
499	114	420	380	340	299	258	217	176	135	94	457	9
500	115	421	381	341	300	259	218	177	136	95	458	10

LOGARITHMS OF NUMBERS

500 — 550

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
500	69	897	506	914	923	932	940	949	958	966	975	1 0.3
501	69	902	511	919	928	937	945	954	962	970	979	2 1.4
502	70	070	072	080	089	097	107	114	122	131	140	3 2.1
503	157	165	174	183	191	200	208	217	226	234	243	4 1.4
504	243	252	260	269	278	286	295	303	312	321		5 2.4
505	329	338	346	355	364	372	381	389	398	406		6 3.4
506	415	424	433	441	450	458	467	475	484	492		7 4.4
507	501	509	518	526	534	543	551	561	569	578		8 5.4
508	586	595	603	612	621	629	638	647	656	665		9 6.4
509	672	680	689	697	706	714	723	731	740	749		1 7.4
510	757	766	774	783	791	800	808	817	825	834		2 8.4
511	842	851	859	868	876	885	894	902	910	919		3 9.4
512	927	935	944	952	961	969	978	986	994	003		4 0.4
513	012	020	029	037	046	054	063	071	079	088		5 1.4
514	096	105	113	122	130	139	147	155	164	172		6 2.4
515	181	189	198	206	214	223	231	240	248	257		7 3.4
516	265	273	282	290	299	307	315	323	332	340		8 4.4
517	349	357	366	374	383	391	399	408	416	425		9 5.4
518	433	441	450	458	466	475	483	492	500	508		1 6.4
519	517	525	533	542	550	559	567	575	584	592		2 7.4
520	600	609	617	625	634	642	650	659	667	675		3 8.4
521	684	692	700	709	717	725	734	742	750	759		4 9.4
522	768	777	784	792	800	809	817	825	834	842		5 0.4
523	850	858	867	875	883	892	900	908	917	925		6 1.4
524	933	941	950	958	966	976	983	991	999	008		7 2.4
525	009	017	024	032	041	049	057	066	074	082		8 3.4
526	090	100	108	116	125	132	140	148	156	165		9 4.4
527	181	189	198	206	213	221	229	237	245	253		1 5.4
528	263	272	280	288	296	304	312	320	329	337		2 6.4
529	346	354	362	370	378	387	395	403	411	419		3 7.4
530	428	436	444	452	460	469	477	485	493	501		4 8.4
531	509	518	526	534	542	550	558	567	575	583		5 9.4
532	591	599	607	616	624	632	640	648	656	665		6 0.4
533	673	681	689	697	705	713	722	730	738	746		7 1.4
534	754	762	770	779	787	795	803	811	819	827		8 2.4
535	835	843	852	859	868	876	884	892	900	908		9 3.4
536	916	925	933	941	949	957	966	974	982	990		1 4.4
537	997	006	014	022	030	038	046	054	062	070		2 5.4
538	081	089	097	105	113	119	127	135	143	151		3 6.4
539	159	167	175	183	191	199	207	215	223	231		4 7.4
540	239	247	255	263	272	280	288	296	304	312		5 8.4
541	320	328	336	344	352	360	368	376	384	392		6 9.4
542	400	408	416	424	432	440	448	456	464	472		7 0.4
543	480	488	496	504	512	520	528	536	544	552		8 1.4
544	560	568	576	584	592	600	608	616	624	632		9 2.4
545	640	648	656	664	672	679	687	695	703	711		1 3.4
546	719	727	735	743	751	758	767	775	783	791		2 4.4
547	799	807	815	823	831	838	846	854	862	870		3 5.4
548	878	886	894	902	910	917	925	933	941	949		4 6.4
549	957	965	973	981	989	997	005	013	020	028		5 7.4
550	74	036	044	052	060	068	076	084	092	099	107	Proportional parts

LOGARITHMS OF NUMBERS

550 — 600

N.	L.									Proportional parts
	0	1	2	3	4	5	6	7	8	
550	74	036	044	052	060	068	076	084	092	099
551	115	123	131	139	147	155	162	170	178	186
552	194	202	210	218	225	233	241	249	257	265
553	273	281	289	297	305	313	320	327	335	343
554	351	359	367	374	382	390	398	406	414	421
555	429	437	445	453	461	468	476	484	492	500
556	507	515	523	531	539	547	554	562	570	578
557	586	594	602	610	618	626	634	642	650	658
558	663	671	679	687	695	703	712	720	728	736
559	741	749	757	764	772	780	788	796	803	811
560	819	827	834	842	850	858	865	873	881	889
561	897	905	913	920	928	936	943	951	958	966
562	974	981	989	997	*004	*012	*020	*028	*036	*043
563	563	571	579	586	594	602	609	617	625	633
564	128	136	143	151	159	166	174	182	189	197
565	205	213	220	228	236	243	251	259	266	274
566	282	289	297	305	312	320	328	335	343	351
567	358	366	374	381	389	397	404	412	420	427
568	435	442	450	458	465	473	481	488	496	504
569	511	519	526	534	542	549	557	565	572	580
570	587	595	603	610	618	626	633	641	648	656
571	664	671	679	686	694	702	709	717	724	732
572	740	747	755	762	770	778	785	793	800	808
573	815	823	831	838	846	853	861	868	876	884
574	891	899	906	914	921	929	937	944	952	959
575	967	974	982	989	997	*005	*012	*020	*027	*035
576	76	042	050	057	065	072	080	087	095	103
577	118	125	133	140	148	155	163	170	178	185
578	193	201	209	217	224	232	240	248	256	264
579	268	275	283	290	298	306	313	320	328	336
580	343	350	358	365	373	380	388	395	403	410
581	418	425	433	440	448	455	462	470	478	485
582	493	501	508	515	523	530	537	545	553	560
583	567	574	582	589	597	604	612	619	626	634
584	641	649	656	664	671	678	686	693	701	708
585	716	723	730	738	745	753	760	768	775	782
586	789	797	804	812	819	827	834	842	849	856
587	864	871	879	886	893	901	908	916	923	930
588	938	945	953	960	967	975	982	989	997	*004
589	77	019	026	034	041	048	056	063	070	078
590	085	093	100	107	115	122	129	137	144	151
591	159	166	173	181	188	195	203	210	217	225
592	232	240	247	254	262	269	276	283	291	298
593	305	313	320	327	333	342	349	357	364	371
594	379	386	393	401	408	415	422	430	437	444
595	452	459	466	474	481	488	495	503	510	517
596	525	532	539	546	554	561	568	576	583	590
597	597	605	612	619	627	634	641	648	656	663
598	670	677	685	692	700	707	715	722	730	737
599	743	750	757	764	772	779	786	793	801	808
600	815	822	830	837	844	851	859	866	873	880

3
6.8
2.1.4
1.2
5.4.0
5.4.0
5.4.0
7.2

7
1.6.7
2.1.4
3.2.4
5.3.5
5.3.5
5.3.5
8.0

Proportional parts

LOGARITHMS OF NUMBERS

600 — 650

N.	1.	0	1	2	3	4	5	6	7	8	9	Proportional parts
600	77	815	822	830	837	844	851	859	868	873	880	1
601	887	895	902	909	916	924	931	939	946	952	959	2
602	967	974	981	988	995	*003	*010	*017	*025	*032	*039	3
603	78	823	830	837	844	851	858	865	872	879	886	4
604	104	111	118	125	132	140	147	154	161	168	175	5
605	175	183	190	197	204	211	219	226	233	240	247	6
606	257	264	271	279	286	293	300	307	314	321	328	7
607	335	343	350	357	364	371	379	386	393	400	407	8
608	380	388	396	403	410	418	425	433	440	447	454	9
609	462	469	476	483	490	497	504	512	519	526	533	10
610	533	540	547	554	561	569	576	583	590	597	604	11
611	604	611	618	625	633	640	647	654	661	668	675	12
612	675	682	689	696	704	711	718	725	732	739	746	13
613	746	753	760	767	774	781	789	796	803	810	817	14
614	817	824	831	838	845	852	859	866	873	880	887	15
615	888	895	902	909	916	923	930	937	944	951	958	16
616	958	965	972	979	986	993	*000	*007	*014	*021	*028	17
617	79	829	836	843	850	857	864	871	878	885	892	18
618	858	865	872	879	886	893	900	906	913	920	927	19
619	189	196	203	210	217	224	231	238	245	252	259	20
620	239	246	253	260	267	274	281	288	295	302	309	21
621	309	316	323	330	337	344	351	358	365	372	379	22
622	389	396	403	410	417	424	431	438	445	452	459	23
623	449	456	463	470	477	484	491	498	505	512	519	24
624	518	525	532	539	546	553	560	567	574	581	588	25
625	588	595	602	609	616	623	630	637	644	650	657	26
626	657	664	671	678	685	692	699	706	713	720	727	27
627	727	734	741	748	754	761	768	775	782	789	796	28
628	796	803	810	817	824	831	837	844	851	858	865	29
629	865	872	879	886	893	900	906	913	920	927	934	30
630	934	941	948	955	962	969	975	982	989	996	003	31
631	80	003	010	017	024	030	037	044	051	058	065	32
632	072	079	085	092	099	106	113	120	127	134	141	33
633	147	154	161	168	175	182	189	195	202	209	216	34
634	259	266	273	280	287	294	301	308	315	322	329	35
635	277	284	291	298	305	312	319	325	332	339	346	36
636	346	353	359	366	373	380	387	393	400	407	414	37
637	421	428	435	442	449	456	463	470	477	484	491	38
638	481	488	495	502	509	516	523	530	537	544	551	39
639	550	557	564	570	577	584	591	598	605	612	619	40
640	618	625	632	638	645	652	659	665	672	679	686	41
641	683	690	696	703	710	717	724	730	737	744	751	42
642	754	760	767	774	781	788	795	802	809	816	823	43
643	821	828	835	841	848	855	862	868	875	882	889	44
644	889	895	902	909	916	922	929	936	943	949	956	45
645	956	963	969	976	983	989	996	*003	*010	*017	*024	46
646	81	023	030	037	043	050	057	064	071	078	085	47
647	090	097	104	111	117	124	131	137	144	151	158	48
648	158	164	171	178	184	191	197	204	211	218	225	49
649	224	231	238	245	251	258	265	271	278	285	292	50
650	291	298	305	311	318	325	332	338	345	351	358	51

.77 615 — .81 351

LOGARITHMS OF NUMBERS

650 — 700

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
650	81	291	298	305	311	318	325	331	338	345	351	
651	398	385	371	378	385	391	398	405	411	418		
652	493	479	465	451	437	423	409	395	381	367		
653	588	574	559	545	531	517	503	489	475	461		
654	683	669	654	639	625	611	597	583	569	555		
655	778	764	749	734	720	706	692	678	664	650		
656	873	859	844	829	815	801	787	773	759	745		
657	968	954	939	925	911	897	883	869	855	841		
658	1063	1049	1034	1020	1006	992	978	964	950	936		
659	1158	1144	1129	1115	1101	1087	1073	1059	1045	1031		
660	1253	1239	1224	1210	1196	1182	1168	1154	1140	1126		
661	1348	1334	1319	1305	1291	1277	1263	1249	1235	1221		
662	1443	1429	1414	1400	1386	1372	1358	1344	1330	1316		
663	1538	1524	1509	1495	1481	1467	1453	1439	1425	1411		
664	1633	1619	1604	1590	1576	1562	1548	1534	1520	1506		
665	1728	1714	1699	1685	1671	1657	1643	1629	1615	1601		
666	1823	1809	1794	1780	1766	1752	1738	1724	1710	1696		
667	1918	1904	1889	1875	1861	1847	1833	1819	1805	1791		
668	2013	1999	1984	1970	1956	1942	1928	1914	1900	1886		
669	2108	2094	2079	2065	2051	2037	2023	2009	1995	1981		
670	2203	2189	2174	2160	2146	2132	2118	2104	2090	2076		
671	2298	2284	2269	2255	2241	2227	2213	2199	2185	2171		
672	2393	2379	2364	2350	2336	2322	2308	2294	2280	2266		
673	2488	2474	2459	2445	2431	2417	2403	2389	2375	2361		
674	2583	2569	2554	2540	2526	2512	2498	2484	2470	2456		
675	2678	2664	2649	2635	2621	2607	2593	2579	2565	2551		
676	2773	2759	2744	2730	2716	2702	2688	2674	2660	2646		
677	2868	2854	2839	2825	2811	2797	2783	2769	2755	2741		
678	2963	2949	2934	2920	2906	2892	2878	2864	2850	2836		
679	3058	3044	3029	3015	3001	2987	2973	2959	2945	2931		
680	3153	3139	3124	3110	3096	3082	3068	3054	3040	3026		
681	3248	3234	3219	3205	3191	3177	3163	3149	3135	3121		
682	3343	3329	3314	3300	3286	3272	3258	3244	3230	3216		
683	3438	3424	3409	3395	3381	3367	3353	3339	3325	3311		
684	3533	3519	3504	3490	3476	3462	3448	3434	3420	3406		
685	3628	3614	3599	3585	3571	3557	3543	3529	3515	3501		
686	3723	3709	3694	3680	3666	3652	3638	3624	3610	3596		
687	3818	3804	3789	3775	3761	3747	3733	3719	3705	3691		
688	3913	3899	3884	3870	3856	3842	3828	3814	3800	3786		
689	4008	3994	3979	3965	3951	3937	3923	3909	3895	3881		
690	4103	4089	4074	4060	4046	4032	4018	4004	3990	3976		
691	4198	4184	4169	4155	4141	4127	4113	4099	4085	4071		
692	4293	4279	4264	4250	4236	4222	4208	4194	4180	4166		
693	4388	4374	4359	4345	4331	4317	4303	4289	4275	4261		
694	4483	4469	4454	4440	4426	4412	4398	4384	4370	4356		
695	4578	4564	4549	4535	4521	4507	4493	4479	4465	4451		
696	4673	4659	4644	4630	4616	4602	4588	4574	4560	4546		
697	4768	4754	4739	4725	4711	4697	4683	4669	4655	4641		
698	4863	4849	4834	4820	4806	4792	4778	4764	4750	4736		
699	4958	4944	4929	4915	4901	4887	4873	4859	4845	4831		
700	5053	5039	5024	5010	4996	4982	4968	4954	4940	4926		

LOGARITHMS OF NUMBERS

700 — 750

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
700	84	510	516	522	528	535	541	547	553	559	566	1 0.7
701	511	517	524	530	537	544	550	556	563	569	576	2 1.4
702	512	518	525	532	539	546	553	560	567	574	581	3 2.1
703	513	519	526	534	541	548	555	562	569	576	583	4 2.8
704	514	520	528	535	543	550	557	564	571	578	585	5 3.5
705	515	522	530	537	545	552	560	567	574	581	588	6 4.2
706	516	524	532	540	548	556	564	572	580	587	595	7 4.9
707	517	525	534	542	550	558	566	574	582	590	598	8 5.6
708	518	526	535	544	552	561	569	577	585	593	601	9 6.3
709	519	528	537	546	555	564	573	582	591	600	608	
710	126	132	138	144	150	156	162	169	175	181	187	1 0.7
711	127	133	139	145	151	157	163	170	176	182	188	2 1.4
712	128	134	140	146	152	158	164	171	177	183	189	3 2.1
713	129	135	141	147	153	159	165	172	178	184	190	4 2.8
714	130	136	142	148	154	160	166	173	179	185	191	5 3.5
715	131	137	143	149	155	161	167	174	180	186	192	6 4.2
716	132	138	144	150	156	162	168	175	181	187	193	7 4.9
717	133	139	145	151	157	163	169	176	182	188	194	8 5.6
718	134	140	146	152	158	164	170	177	183	189	195	9 6.3
719	135	141	147	153	159	165	171	178	184	190	196	
720	733	738	745	751	757	763	769	775	781	788	794	
721	734	739	746	752	758	764	770	776	782	788	794	1 0.7
722	735	740	747	753	759	765	771	777	783	789	795	2 1.4
723	736	741	748	754	760	766	772	778	784	790	796	3 2.1
724	737	742	749	755	761	767	773	779	785	791	797	4 2.8
725	738	743	750	756	762	768	774	780	786	792	798	5 3.5
726	739	744	751	757	763	769	775	781	787	793	799	6 4.2
727	740	745	752	758	764	770	776	782	788	794	800	7 4.9
728	741	746	753	759	765	771	777	783	789	795	801	8 5.6
729	742	747	754	760	766	772	778	784	790	796	802	9 6.3
730	332	338	344	350	356	362	368	374	380	386	392	
731	333	339	345	351	357	363	369	375	381	387	393	1 0.7
732	334	340	346	352	358	364	370	376	382	388	394	2 1.4
733	335	341	347	353	359	365	371	377	383	389	395	3 2.1
734	336	342	348	354	360	366	372	378	384	390	396	4 2.8
735	337	343	349	355	361	367	373	379	385	391	397	5 3.5
736	338	344	350	356	362	368	374	380	386	392	398	6 4.2
737	339	345	351	357	363	369	375	381	387	393	399	7 4.9
738	340	346	352	358	364	370	376	382	388	394	400	8 5.6
739	341	347	353	359	365	371	377	383	389	395	401	9 6.3
740	342	348	354	360	366	372	378	384	390	396	402	
741	343	349	355	361	367	373	379	385	391	397	403	1 0.7
742	344	350	356	362	368	374	380	386	392	398	404	2 1.4
743	345	351	357	363	369	375	381	387	393	399	405	3 2.1
744	346	352	358	364	370	376	382	388	394	400	406	4 2.8
745	347	353	359	365	371	377	383	389	395	401	407	5 3.5
746	348	354	360	366	372	378	384	390	396	402	408	6 4.2
747	349	355	361	367	373	379	385	391	397	403	409	7 4.9
748	350	356	362	368	374	380	386	392	398	404	410	8 5.6
749	351	357	363	369	375	381	387	393	399	405	411	9 6.3
750	506	512	518	523	529	535	541	547	552	558	563	Proportional parts

LOGARITHMS OF NUMBERS.

750 — 800

N.	0	1	2	3	4	5	6	7	8	9	Proportional parts
750	87	506	512	518	523	529	535	541	547	552	558
751	664	570	576	581	587	593	599	604	610	616	
752	682	628	633	639	645	651	656	662	668	674	
753	681	637	643	649	655	661	667	673	679	685	
754	737	743	749	754	760	766	772	777	783	789	
755	795	800	806	812	818	823	829	835	841	846	
756	852	858	864	869	875	881	887	892	898	904	
757	911	917	923	928	934	939	945	951	956	961	
758	967	973	978	984	990	996	1002	1007	1013	1018	
759	88	024	030	036	041	047	053	058	064	070	
760	088	087	093	098	104	110	116	121	127	133	6
761	144	143	148	154	160	166	172	178	184	190	1
762	199	201	207	213	218	224	230	236	242	248	2
763	282	288	294	299	305	311	317	323	329	335	3
764	309	315	321	326	332	338	343	349	355	360	4
765	366	372	377	383	389	395	400	406	412	417	5
766	423	429	434	440	446	451	457	463	468	474	6
767	480	485	491	497	502	508	513	519	525	530	7
768	536	542	547	553	559	564	570	576	581	587	8
769	593	598	604	610	616	621	627	632	638	643	9
770	649	655	660	666	672	677	683	689	694	700	
771	705	711	717	722	728	734	739	745	750	756	
772	762	767	773	779	784	790	795	801	807	812	
773	818	824	829	835	840	846	852	857	863	868	
774	874	880	885	891	897	902	908	913	919	925	
775	930	936	941	947	953	958	964	969	975	981	
776	986	992	997	*003	*009	*014	*020	*025	*031	*037	
777	89	042	048	053	059	064	070	076	081	087	
778	100	106	112	118	123	129	135	141	147	153	
779	154	159	165	170	176	182	187	193	198	204	
780	209	215	221	226	232	237	243	248	254	260	
781	265	271	276	282	287	293	298	304	310	315	
782	321	327	332	337	343	348	354	359	365	370	
783	376	382	387	393	398	404	409	415	421	426	
784	432	437	443	448	454	459	465	470	476	481	
785	487	492	498	504	509	515	520	526	531	537	
786	542	548	553	559	564	569	575	580	586	591	
787	597	603	609	614	620	625	631	636	642	647	
788	653	658	664	669	675	680	686	691	697	702	
789	708	713	719	724	730	735	741	746	752	757	
790	763	768	774	779	785	790	796	801	807	812	
791	818	823	829	834	840	845	851	856	862	867	
792	873	878	883	889	894	900	905	911	916	922	
793	927	933	938	944	949	955	960	966	971	977	
794	982	988	993	*004	*009	*015	*020	*026	*031		
795	90	037	042	048	053	059	064	069	075	080	
796	091	097	102	108	113	119	124	129	135	140	
797	146	151	157	162	168	173	179	184	189	195	
798	199	205	211	216	222	227	233	238	244	250	
799	255	260	266	271	276	282	287	293	298	304	
800	309	314	320	325	331	336	342	347	352	358	

5
1 1.6
2 1.6
3 1.6
4 1.6
5 1.6
6 1.6
7 1.6
8 1.6
9 1.6

6
1 1.6
2 1.6
3 1.6
4 1.6
5 1.6
6 1.6
7 1.6
8 1.6
9 1.6

LOGARITHMS OF NUMBERS

800 — 850

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
800	90	309	314	320	325	331	336	342	347	352	358	1 0.6
801	309	314	320	325	331	336	342	347	352	358	364	1 1.2
802	309	314	320	325	331	336	342	347	352	358	364	1 1.8
803	309	314	320	325	331	336	342	347	352	358	364	1 2.4
804	309	314	320	325	331	336	342	347	352	358	364	1 3.0
805	309	314	320	325	331	336	342	347	352	358	364	1 3.6
806	309	314	320	325	331	336	342	347	352	358	364	1 4.2
807	309	314	320	325	331	336	342	347	352	358	364	1 4.8
808	309	314	320	325	331	336	342	347	352	358	364	1 5.4
809	309	314	320	325	331	336	342	347	352	358	364	1 6.0
810	309	314	320	325	331	336	342	347	352	358	364	1 6.6
811	309	314	320	325	331	336	342	347	352	358	364	1 7.2
812	309	314	320	325	331	336	342	347	352	358	364	1 7.8
813	309	314	320	325	331	336	342	347	352	358	364	1 8.4
814	309	314	320	325	331	336	342	347	352	358	364	1 9.0
815	309	314	320	325	331	336	342	347	352	358	364	1 9.6
816	309	314	320	325	331	336	342	347	352	358	364	1 10.2
817	309	314	320	325	331	336	342	347	352	358	364	1 10.8
818	309	314	320	325	331	336	342	347	352	358	364	1 11.4
819	309	314	320	325	331	336	342	347	352	358	364	1 12.0
820	309	314	320	325	331	336	342	347	352	358	364	1 12.6
821	309	314	320	325	331	336	342	347	352	358	364	1 13.2
822	309	314	320	325	331	336	342	347	352	358	364	1 13.8
823	309	314	320	325	331	336	342	347	352	358	364	1 14.4
824	309	314	320	325	331	336	342	347	352	358	364	1 15.0
825	309	314	320	325	331	336	342	347	352	358	364	1 15.6
826	309	314	320	325	331	336	342	347	352	358	364	1 16.2
827	309	314	320	325	331	336	342	347	352	358	364	1 16.8
828	309	314	320	325	331	336	342	347	352	358	364	1 17.4
829	309	314	320	325	331	336	342	347	352	358	364	1 18.0
830	309	314	320	325	331	336	342	347	352	358	364	1 18.6
831	309	314	320	325	331	336	342	347	352	358	364	1 19.2
832	309	314	320	325	331	336	342	347	352	358	364	1 19.8
833	309	314	320	325	331	336	342	347	352	358	364	1 20.4
834	309	314	320	325	331	336	342	347	352	358	364	1 21.0
835	309	314	320	325	331	336	342	347	352	358	364	1 21.6
836	309	314	320	325	331	336	342	347	352	358	364	1 22.2
837	309	314	320	325	331	336	342	347	352	358	364	1 22.8
838	309	314	320	325	331	336	342	347	352	358	364	1 23.4
839	309	314	320	325	331	336	342	347	352	358	364	1 24.0
840	309	314	320	325	331	336	342	347	352	358	364	1 24.6
841	309	314	320	325	331	336	342	347	352	358	364	1 25.2
842	309	314	320	325	331	336	342	347	352	358	364	1 25.8
843	309	314	320	325	331	336	342	347	352	358	364	1 26.4
844	309	314	320	325	331	336	342	347	352	358	364	1 27.0
845	309	314	320	325	331	336	342	347	352	358	364	1 27.6
846	309	314	320	325	331	336	342	347	352	358	364	1 28.2
847	309	314	320	325	331	336	342	347	352	358	364	1 28.8
848	309	314	320	325	331	336	342	347	352	358	364	1 29.4
849	309	314	320	325	331	336	342	347	352	358	364	1 30.0
850	309	314	320	325	331	336	342	347	352	358	364	1 30.6

LOGARITHMS OF NUMBERS

850 — 900

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
850	92	942	947	952	957	962	967	973	978	983	988	1
851	92	944	949	954	959	964	969	975	980	985	990	1.1
852	93	044	049	054	059	064	069	075	080	085	090	1.2
853	93	095	100	105	110	115	121	126	131	136	141	1.3
854	94	146	151	156	161	166	171	176	181	186	191	1.4
855	94	197	202	207	212	217	222	227	232	237	242	1.5
856	94	247	252	257	262	267	272	277	282	287	292	1.6
857	94	298	303	308	313	318	323	328	333	338	343	1.7
858	95	349	354	359	364	369	374	379	384	389	394	1.8
859	95	399	404	409	414	420	425	430	435	440	445	1.9
860	95	450	455	460	465	470	475	480	485	490	495	2
861	95	500	505	510	515	520	526	531	536	541	546	2.1
862	95	551	556	561	566	571	576	581	586	591	596	2.2
863	95	601	606	611	616	621	626	631	636	641	646	2.3
864	95	651	656	661	666	671	676	682	687	692	697	2.4
865	95	702	707	712	717	722	727	732	737	742	747	2.5
866	95	752	757	762	767	772	777	782	787	792	797	2.6
867	95	807	812	817	822	827	832	837	842	847	852	2.7
868	95	857	862	867	872	877	882	887	892	897	902	2.8
869	95	902	907	912	917	922	927	932	937	942	947	2.9
870	95	952	957	962	967	972	977	982	987	992	997	3
871	96	002	007	012	017	022	027	032	037	042	047	3.1
872	96	052	057	062	067	072	077	082	087	092	097	3.2
873	96	101	106	111	116	121	126	131	136	141	146	3.3
874	96	151	156	161	166	171	176	181	186	191	196	3.4
875	96	201	206	211	216	221	226	231	236	240	245	3.5
876	96	250	255	260	265	270	275	280	285	290	295	3.6
877	96	300	305	310	315	320	325	330	335	340	345	3.7
878	96	349	354	359	364	369	374	379	384	389	394	3.8
879	96	399	404	409	414	419	424	429	433	438	443	3.9
880	96	448	453	458	463	468	473	478	483	488	493	4
881	96	498	503	507	512	517	522	527	532	537	542	4.1
882	96	547	552	557	562	567	571	576	581	586	591	4.2
883	96	596	601	606	611	616	621	626	630	635	640	4.3
884	96	645	650	655	660	665	670	675	680	685	690	4.4
885	96	694	699	704	709	714	719	724	729	734	738	4.5
886	96	743	748	753	758	763	768	773	778	783	788	4.6
887	96	793	798	803	808	813	818	823	828	833	838	4.7
888	96	841	846	851	856	861	866	871	876	881	886	4.8
889	96	890	895	900	905	910	915	919	924	929	934	4.9
890	96	939	944	949	954	959	963	968	973	978	983	5
891	96	989	994	999	004	009	013	018	023	028	033	5.1
892	95	036	041	046	051	056	061	066	071	076	080	5.2
893	95	085	090	095	100	105	109	114	119	124	129	5.3
894	95	134	139	143	148	153	158	163	168	173	177	5.4
895	95	187	192	197	202	207	211	216	221	226	231	5.5
896	95	231	236	240	245	250	255	260	265	270	274	5.6
897	95	279	284	289	294	299	303	308	313	318	323	5.7
898	95	328	332	337	342	347	352	357	361	366	371	5.8
899	95	376	381	386	390	395	400	405	410	415	419	5.9
900	95	424	429	434	439	444	448	453	458	463	468	6
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

LOGARITHMS OF NUMBERS

900 — 950

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
900	95	424	429	434	439	444	448	453	458	463	468	1
901	572	477	482	487	492	497	501	506	511	516	521	2
902	573	478	483	488	493	498	503	508	513	518	523	3
903	569	574	578	583	588	593	598	603	607	612	617	4
904	617	622	626	631	636	641	646	650	655	660	665	5
905	665	670	674	679	684	689	694	698	703	708	713	6
906	717	722	726	731	736	741	746	750	755	760	765	7
907	766	771	775	780	785	790	795	799	804	809	814	8
908	809	813	818	823	828	833	837	842	847	852	857	9
909	856	861	866	871	875	880	885	890	895	899		
910	904	909	914	918	923	928	933	938	942	947	952	1
911	952	957	961	966	971	976	980	985	989	994	999	2
912	999	*004	*009	*014	*019	*023	*028	*033	*038	*042		3
913	98	047	052	057	061	066	071	076	080	085	090	4
914	095	099	104	109	114	118	123	128	133	137		5
915	142	147	152	156	161	166	171	175	180	185	190	6
916	190	194	199	204	209	213	218	223	227	232	237	7
917	237	242	246	251	256	261	265	270	275	280	285	8
918	284	289	294	298	303	308	313	317	322	327	332	9
919	332	336	341	346	350	355	360	365	369	374		
920	379	384	388	393	398	402	407	412	417	421	426	1
921	426	431	435	440	445	450	454	459	464	468	473	2
922	473	478	483	487	492	497	501	506	511	515	520	3
923	520	525	530	534	539	544	548	553	558	562	567	4
924	567	572	577	581	586	591	595	600	605	609	614	5
925	614	619	624	628	633	638	642	647	652	656	661	6
926	661	666	670	675	680	685	689	694	699	703	708	7
927	708	713	717	722	727	731	736	741	745	750	755	8
928	759	764	769	774	778	783	788	792	797	802	807	9
929	802	806	811	816	820	825	830	834	839	844		
930	848	853	858	862	867	872	876	881	886	890	895	1
931	895	900	904	909	914	918	923	928	932	937	942	2
932	946	951	955	960	965	970	974	979	984	988	993	3
933	998	993	998	003	007	012	017	022	026	031	036	4
934	97	038	043	047	052	056	061	065	070	075	079	5
935	081	086	090	095	100	104	109	114	118	123	127	6
936	128	132	137	142	146	151	155	160	165	169	174	7
937	179	183	188	192	197	201	206	211	215	220	225	8
938	229	233	238	243	247	252	257	261	266	271	275	9
939	267	271	276	280	285	290	294	299	304	308		
940	318	317	322	327	331	336	340	345	350	354	359	1
941	358	362	367	371	376	380	385	389	394	398	403	2
942	405	410	414	419	424	428	433	437	442	446	451	3
943	451	456	460	465	470	474	479	483	488	493	497	4
944	497	502	506	511	516	520	525	529	534	539	543	5
945	548	552	557	562	567	571	576	580	585	590	594	6
946	598	603	607	612	617	621	626	631	635	640	645	7
947	648	653	657	662	667	671	676	681	685	690	695	8
948	698	703	707	712	717	721	726	731	735	740	745	9
949	749	754	759	763	768	773	777	782	786	791		
950	795	800	804	809	813							

LOGARITHMS OF NUMBERS

950 — 1000

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
950	97	772	777	782	786	791	795	800	804	809	813	1
951	80	773	778	783	787	792	796	801	805	810	814	2
952	83	774	779	784	788	793	797	802	806	811	815	3
953	86	775	780	785	789	794	798	803	807	812	816	4
954	89	776	781	786	790	795	799	804	808	813	817	5
955	92	777	782	787	791	796	800	805	809	814	818	6
956	95	778	783	788	792	797	801	806	810	815	819	7
957	98	779	784	789	793	798	802	807	811	816	820	8
958	01	780	785	790	794	799	803	808	812	817	821	9
959	04	781	786	791	795	800	804	809	813	818	822	10
960	07	782	787	792	796	801	805	810	814	819	823	11
961	10	783	788	793	797	802	806	811	815	820	824	12
962	13	784	789	794	798	803	807	812	816	821	825	13
963	16	785	790	795	799	804	808	813	817	822	826	14
964	19	786	791	796	800	805	809	814	818	823	827	15
965	22	787	792	797	801	806	810	815	819	824	828	16
966	25	788	793	798	802	807	811	816	820	825	829	17
967	28	789	794	799	803	808	812	817	821	826	830	18
968	31	790	795	800	804	809	813	818	822	827	831	19
969	34	791	796	801	805	810	814	819	823	828	832	20
970	37	792	797	802	806	811	815	820	824	829	833	21
971	40	793	798	803	807	812	816	821	825	830	834	22
972	43	794	799	804	808	813	817	822	826	831	835	23
973	46	795	800	805	809	814	818	823	827	832	836	24
974	49	796	801	806	810	815	819	824	828	833	837	25
975	52	797	802	807	811	816	820	825	829	834	838	26
976	55	798	803	808	812	817	821	826	830	835	839	27
977	58	799	804	809	813	818	822	827	831	836	840	28
978	61	800	805	810	814	819	823	828	832	837	841	29
979	64	801	806	811	815	820	824	829	833	838	842	30
980	67	802	807	812	816	821	825	830	834	839	843	31
981	70	803	808	813	817	822	826	831	835	840	844	32
982	73	804	809	814	818	823	827	832	836	841	845	33
983	76	805	810	815	819	824	828	833	837	842	846	34
984	79	806	811	816	820	825	829	834	838	843	847	35
985	82	807	812	817	821	826	830	835	839	844	848	36
986	85	808	813	818	822	827	831	836	840	845	849	37
987	88	809	814	819	823	828	832	837	841	846	850	38
988	91	810	815	820	824	829	833	838	842	847	851	39
989	94	811	816	821	825	830	834	839	843	848	852	40
990	97	812	817	822	826	831	835	840	844	849	853	41
991	00	813	818	823	827	832	836	841	845	850	854	42
992	03	814	819	824	828	833	837	842	846	851	855	43
993	06	815	820	825	829	834	838	843	847	852	856	44
994	09	816	821	826	830	835	839	844	848	853	857	45
995	12	817	822	827	831	836	840	845	849	854	858	46
996	15	818	823	828	832	837	841	846	850	855	859	47
997	18	819	824	829	833	838	842	847	851	856	860	48
998	21	820	825	830	834	839	843	848	852	857	861	49
999	24	821	826	831	835	840	844	849	853	858	862	50
1000	27	822	827	832	836	841	845	850	854	859	863	51

INTERNATIONAL ATOMIC WEIGHTS 1941

	Sym- bol	No.	Atomic Weight		Sym- bol	No.	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

Index

A

Absolute density of water, 126
Acids, normal solutions of, 116
Acids, stock solutions of, 113
Acid-base equations, 122
Acid-base indicators, 17
Acid-base indicators, stock solutions of, 112
Acid-base standards, 119
Acid-base volumetric factors, logarithms of, 124
Activin. See Chloramine T
Adipic acid, 39
Adsorption indicators, 10
Amines, sulphuric acid salts of aromatic, 39
Aminosulphonic acid, 39
Ammonia, standardization of, 61
Ammonium thiocyanate, 67
Ammonium thiocyanate, standardization of, 64
Ammonium triiodate, 36, 44
Aniline, 93
Arsenious acid, 44, 93, 105, 106
Arsenious oxide, 73, 97
Arsenious oxide, standardization of, 91, 92
Atomic weights, 146

B

Barium chloride, 55
Barium hydroxide, standardization of, 61

Bases, normal solutions, of, 116
Bases, stock solutions of, 114
Benzoic acid, 38, 59
Boiling points for the calibration of thermometers, 127
Borax, 32, 52
Boric acid, 36
Bromocyanogen, 36
Buoyancy in preparing standard solutions, 6
Burettes, 12
Burettes, calibration of, 14

C

Cadmium sulphate, 37
Calcium hypochlorite, 105
Calcium oxalate, 45
Calibration of burettes, 14
Calibration of flasks, 13
Calibration of pipettes, 14
Calibration of thermometers, 127
Calibration of volumetric apparatus, 11
Carbon dioxide removal, 51, 54
Carbonate removal, 61
Ceric sulphate, standardization of, 95
Checking standardization, 8
Chloramine T, standardization of, 104
Classification of the reaction, 19
Cleaning of apparatus, 12
Constant-boiling hydrochloric acid, preparation of, 48

Copper, 42, 80
Copper salts, 80
Cubical expansion of glass, coefficient of, 5, 13
Cubical expansion of Pyrex glass, 13

D

Definitions, 1
Density of water, absolute, 126
Dilution of standard solutions, 4
Diphenylamine, 25, 112
Diphenylbenzidine, 26, 112
Diphenylguanidine, 33
Dipotassium periodate, 34

E

Electrode potential, 23
Electron transfer, 3
End point, 10
Equations involved in standardization, 122
Equivalent reacting weight, 2
Equivalent weight, definition of, 1
Errors in standardization, 8

F

Ferric ammonium alum, 65, 66
Ferric ammonium sulphate, 46, 113
Ferric nitrate, 113
Ferrous ammonium sulphate, 86, 111
Ferrous ammonium sulphate, standardization of, 90
Ferrous o-phenanthroline, 112
Ferrous sulphate, 85, 98
Ferrous sulphate, standardization of, 90
Flasks, calibration of, 13
Flasks, volumetric, 11
Fuoric acid, 39

G

Glass, coefficient of cubical expansion of, 5
Guanidine carbonate, 33

H

Hanus solution, standardization of, 102
Hydration temperatures for the calibration of thermometers, 127
Hydrazine, 44
Hydrazine sulphate, 44
Hydrochloric acid, 58
Hydrochloric acid, precipitation as silver chloride, 52
Hydrochloric acid, preparation of constant-boiling, 48
Hydrochloric acid, standardization of, 48
Hypochlorite solutions, standardization of, 105

I

Indicator, choice of, 9
Indicators, classification of, 16
Indicators, definition of, 16
Indicators, general discussion of, 28
Indicators for precipitation reactions, 27
Indicators, stock solutions of, 112
International atomic weights, 146
Iodine, 76, 91, 92
Iodine, standardization of, 71
Iron wire, 85

L

Labelling standard solutions, 5
Laboratory reagents, stock solutions of, 113

Logarithms of numbers, 128
Logarithms of volumetric factors, 124

M

Malonic acid, 38
Manganic sulphate, standardization of, 111
Melting points for the calibration of thermometers, 127
Mercuric oxide, yellow, 35
Methyl orange, 21, 112
Methyl red, 22, 112
Methyl yellow, 21, 112
Milliequivalent, definition of, 9
Miscellaneous solutions, 114
Miscellaneous standard solutions, 101
Mohr's salt, 85, 98

N

Normal solutions of acids and bases, 116
Normal solutions of oxidizing and reducing agents, 117
Normal solutions of precipitating agents, 118
Normality, calculating, 9

O

Organic standards, 38
Ortho-phenanthroline complex, 26
Oxalic acid, 42, 45, 82, 95, 96
Oxidation-reduction equations, 2, 122
Oxidation-reduction indicators, 10, 23
Oxidation-reduction indicators, stock solutions of, 112
Oxidation-reduction standards, 120
Oxidation-reduction volumetric factors, logarithms of, 125

Oxidizing agents, normal solutions of, 117
Oxidizing reagents, standard solutions of, 71

P

Parallax in reading, 15
Phenolphthalein, 20, 112
Phthalic acid, 38
Phthalic anhydride, 38
Picric acid, 56
Pipettes, 11
Pipettes, calibration of, 14
Potassium acid phthalate, 58
Potassium bicarbonate, 33
Potassium biiodate, 42, 59
Potassium binoxalate, 37
Potassium bromate, 41, 77
Potassium bromate, standardization of, 92
Potassium chlorate, 37
Potassium chromate, 113
Potassium dichromate, 40, 78, 90, 109
Potassium dichromate, standardization of, 86
Potassium hydroxide, standardization of, 60
Potassium iodate, 41
Potassium iodate, standardization of, 94
Potassium iodide, 42, 47, 84
Potassium permanganate, 42, 90
Potassium permanganate, standardization of, 81
Potassium stannous diquatetratechloride, 44, 45
Potassium thiocyanate, standardization of, 64
Precipitating agents, normal solutions of, 118
Precipitation equations, 123
Precipitation indicators, stock solutions of, 113
Precipitation reactions, indicators for, 27



Precipitation reagents, standard solutions of, 64
 Precipitation standards, 121
 Precipitation volumetric factors, logarithms of, 126
 Primary standards, 7, 8, 119
 Pyrex glass, cubical expansion of, 13

R

Reacting weight, 2
 Reaction, classification of the, 19
 Reading errors, 15
 Reagents, stock solutions of laboratory, 113
 Reducing agents, normal solutions of, 117
 References, 127
 References, supplementary, 30, 63, 70, 99, 111

S

Salicylic acid, 39
 Silver, metallic, 45
 Silver nitrate, 44, 65
 Silver nitrate, standardization of, 66
 Sodium acetomercurithymol sulphate, 44
 Sodium carbonate, 50
 Sodium carbonate, anhydrous, 32
 Sodium chloride, 66
 Sodium chlorite, standardization of, 107
 Sodium hydroxide, standardization of, 57
 Sodium oxalate, 45, 82, 95, 96
 Sodium thiosulphate, 44, 71, 86, 92, 94, 102, 103, 106, 108
 Sodium thiosulphate, standardization of, 75
 Sørensen's "oily alkali," 57
 Standards, primary, 119
 Standard solutions, 4

Standard solutions, miscellaneous, 101
 Standard substances, 31
 Starch solution, 26
 Stock solutions of indicators, 112
 Stock solutions of laboratory reagents, 113
 Storing standard solutions, 5
 Succinic acid, 38
 Succinic anhydride, 38
 Sulphamic acid, 39
 Sulphuric acid, standardization of, 55
 Supplementary references, 30, 63, 70, 99, 111

T

Tables, 116
 Temperature, calibrating, 12
 Temperature changes, correction of standard solutions according to, 5
 Thallous carbonate, 34, 54, 95
 Thermometers, calibration of, 127
 Thiosulphate. See sodium thiosulphate
 Thymol blue, 22, 112
 Titanium sulphate, standardization of, 108
 Titanium trichloride, standardization of, 108
 Tolamine. See Chloramine T

U

Universal primary standard, 31, 36
 Uranyl acetate, 113

V

Volumetric apparatus, calibration of, 11
 Volumetric factors, logarithms of, 124

W

Water, absolute density of, 126

Weighing correction, 8

Weighing error, 6

Weight in vacuo, 7, 13

Wijs' solution, standardization
of, 101

Z

Zinc oxide, 40

